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Carbon-Carbon Bond Manipulation Using First Row Transition Metals

by

James S. M. Sochan



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of Masters of Science.

Department of Chemistry

Edmonton, Alberta

Fall 2003



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Abstract

Known η^5 -cyclohexadienyl iron(II) and η^4 -cyclopentadienyl iron(II) sandwich complexes were investigated for their ability to promote carbon-carbon bond activation. This activity was observed for each template selected, however, the poor binding affinity of the six membered ring ligands resulted in low yields of the desired organometallic products.

The same iron(II) sandwich complexes were protonated in the presence of various alkynes in the hope of obtaining cyclopentenyl/alkyne cycloaddition products. This cycloaddition has been demonstrated for complexes of both cobalt and ruthenium. Unfortunately, no analogous cycloadducts were found for any iron template assayed to promoted this cycloaddition.

In the second part of this thesis, two synthetic pathways were developed to synthesize bis(alkylbromide) substrates with both allyl and primary terminal bromide functionality. Of the two pathways, the procedure involving a ruthenium-catalyzed olefin metathesis step developed by Grubbs produced higher overall yields.

These substrates were then used to evaluate the bis(1,3-dimethylindenyl)titanium chloride complex for the ability to mediate the formation of bicyclic titanacyclobutanes by radical alkylation. Using a one-pot method developed by the Stryker group, 1,1'-[bis(1,3-dimethylindenyl)] titanabicyclo[4.2.0]octane **36** and 1,1'-[bis(1,3-dimethylindenyl)] titanabicyclo[5.2.0]nonane **37** were both synthesized in good yield. Both complexes were obtained as a single stereo isomer but the stereochemistry at the ring junction has not yet been unambiguously determined.

To my wonderful wife Sonya

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List of Abbreviations

Bn	benzene
Cp	η^5 -cyclopentadienyl
Cp*	η^5 -pentamethylcyclopentadienyl
DiBAH	diisobutylaluminum hydride
EHMO	extended Huckel Molecular orbital calculations
Et	ethyl group
HMQC	heteronuclear multiple quantum coherence
HOMO	highest occupied molecular orbital
Hz	hertz
<i>i</i> Pr	<i>iso</i> -propyl
L	ligand
LUMO	lowest unoccupied molecular orbital
M	metal
Me	methyl
MO	molecular orbital
NMR	nuclear magnetic resonance
Ph	phenyl
R	alkyl group
SOMO	singly occupied molecular orbital
<i>t</i> Bu	<i>tert</i> -butyl
THF	tetrahydrofuran

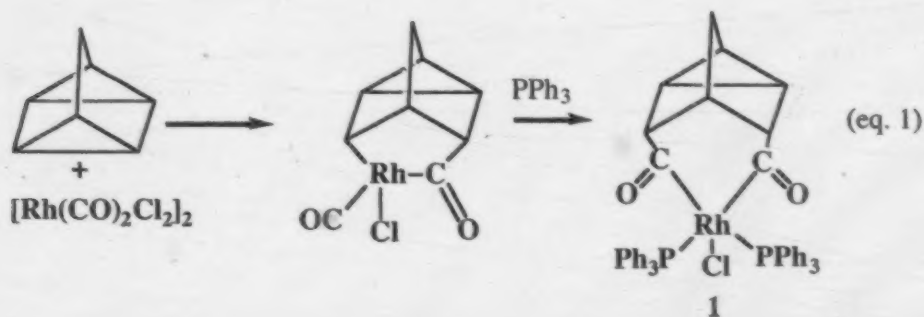
Chapter 1 Carbon-Carbon Bond Activation in Cationic Iron

Cyclohexadienyl Complexes

Chapter 1.1: Introduction to Carbon-Carbon Bond Activation

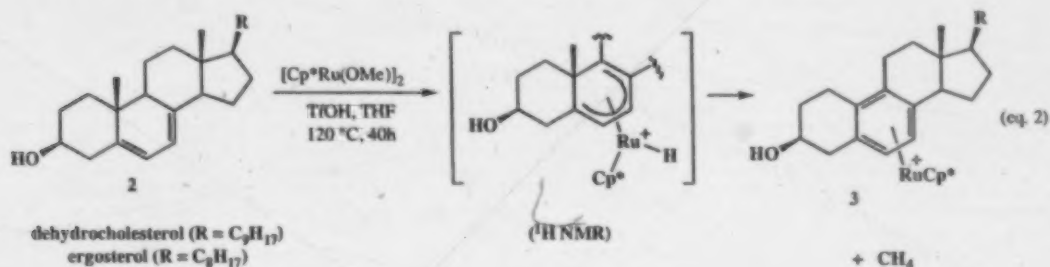
Selective activation of carbon-carbon and carbon-hydrogen bonds is an interesting and challenging problem for the modern chemist. Of the two areas, carbon-hydrogen bond activation is more easily accomplished and there are thus many more examples of this process in the literature. This trend can be explained by some of the following properties: sterically, it is easier to approach a C-H bond; most organic molecules have more C-H bonds; carbon-carbon bonds are usually stronger and less polarized than C-H bonds.¹ In order to overcome these problems, chemists have resorted to a number of strategies, using special systems that have greatly lowered activation barriers.

One method involves oxidative addition of a C-C bond across a metal driven by release of ring strain.² An early example using $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was demonstrated by Cassar and Halpern. In this example, some of the ring strain of quadricyclene is released by the oxidative addition of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ into one of the strained carbon-carbon bonds to form **1** (eq. 1).

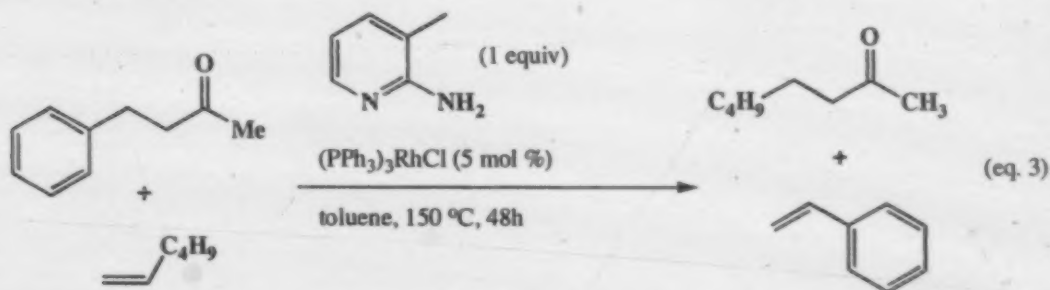


A second typical method involves inducing a β -alkyl elimination from an alkylated η^4 -cyclopentadiene or η^5 -cyclohexadienyl ligand to yield, respectively, an η^5 -cyclopentadiene or η^6 -arene complex. The activation barrier in these processes is lowered by the formation of new aromatic rings in the products.^{3,4} A useful example

involves the demethylation of an unsaturated steroid **2** to form a new aromatic ring within the steroid (eq 2).⁵

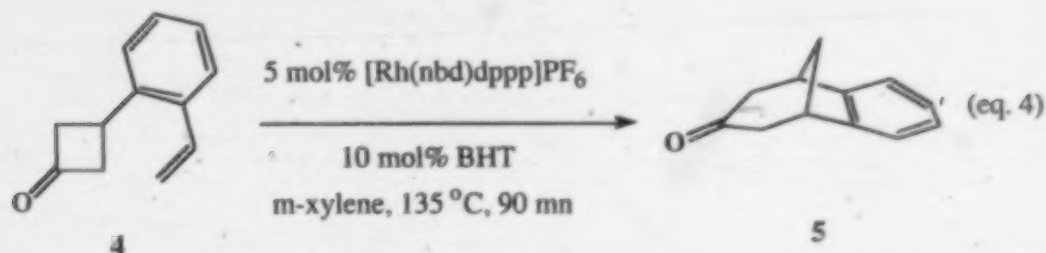


A third type of C-C activation was first developed by Suggs, *et al.* This process involves an oxidative C-C activation using proximity effects to compete with the otherwise more favorable C-H activation. The work done by Suggs and those that followed all involved stoichiometric reactions,⁶ but recently, a catalytic variant of this proximity effect has been described by Jun, *et al.* In this work, a rhodium-based catalyst was employed, along with 2-amino-3-picoline to convert benzylacetone and 1-hexene to 2-octenone (eq. 3).⁷

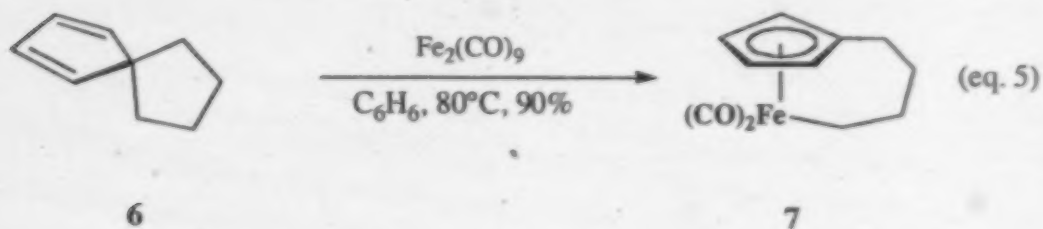


A combination of effects can also be used to promote a carbon-carbon activation event. Recently an interesting example of this was reported by Murakami, *et al.*,⁸ involving the insertion of low valent rhodium into the α -carbon of cyclobutanone **4**, followed by olefin insertion and reductive elimination to furnish bicyclo[3.2.1]octanone **5** (eq. 4). This reaction relieves the ring strain of the four-membered ring, but in order for

this to occur, it appears to also require coordination of the carbonyl, which directs the carbon-carbon bond cleavage.⁸

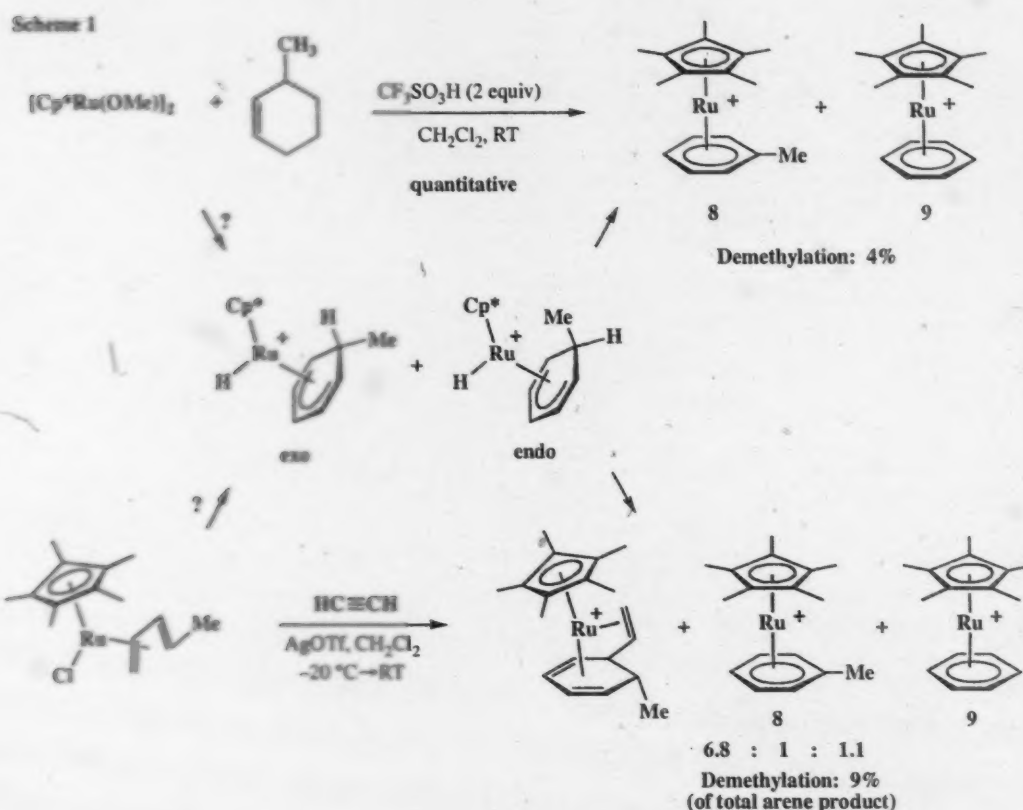


The examples above all use second and third row transition metals to activate the C-C bonds; there are considerably fewer examples utilizing first row transition metals. First row metals do not generally undergo oxidative insertion as easily as second and third row metals, being less electron-rich. In addition, first row metals have much smaller ionic radii, so the coordination sphere is correspondingly more crowded. One example that does use a lower valent first row transition metal has been reported by Eilbracht, *et al.* $[\text{Fe}_2(\text{CO})_9]$ reacts with spirocyclopentadiene **6** to cleave one of the carbon-carbon bonds, giving the new aromatic substituted cyclopentadiene ring **7** (eq. 5).⁹



I. Carbon-Carbon Bond Activation of Cationic 6-Alkylcyclohexadienyl Ruthenium Hydride Complexes.

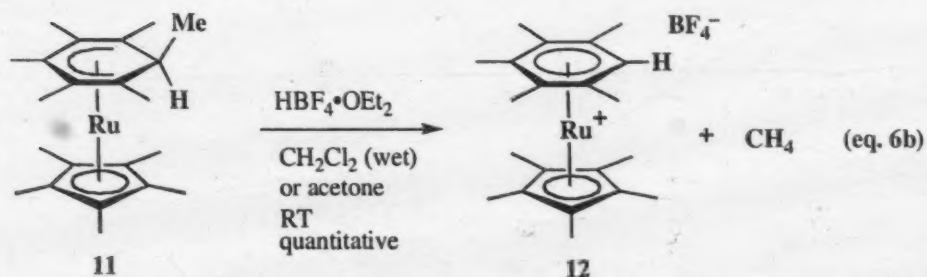
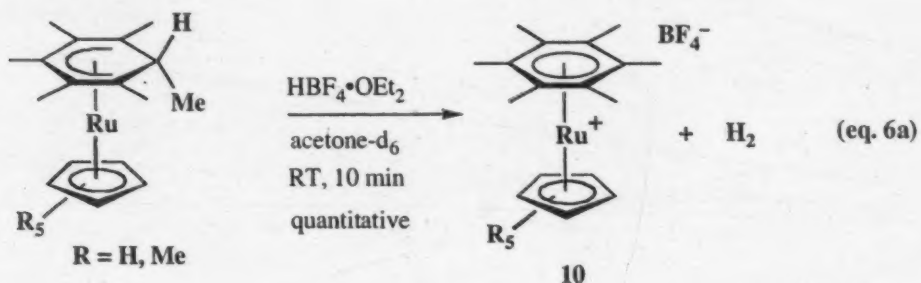
The formation of aromatic rings is the driving force for many types of chemical reactions. Itoh and Chaudret each discovered a ring forming reaction, in part involving carbon-carbon bond activation (Scheme 1), which produces rings with aromatic character to them. Chaudret produces toluene and η^6 -benzene complexes of ruthenium 8 and 9, respectively, starting from 3-methylcyclohexene.¹⁰ In Itoh's chemistry, a small amount of the benzene ruthenium product is generated during metal-mediated diene/alkyne cycloadditions.¹¹



To explain these reactions, Chaudret and Itoh both propose the formation of 1-*exo* and 1-*endo* η^5 -cyclohexadienyl intermediates as illustrated. They suggest that carbon-

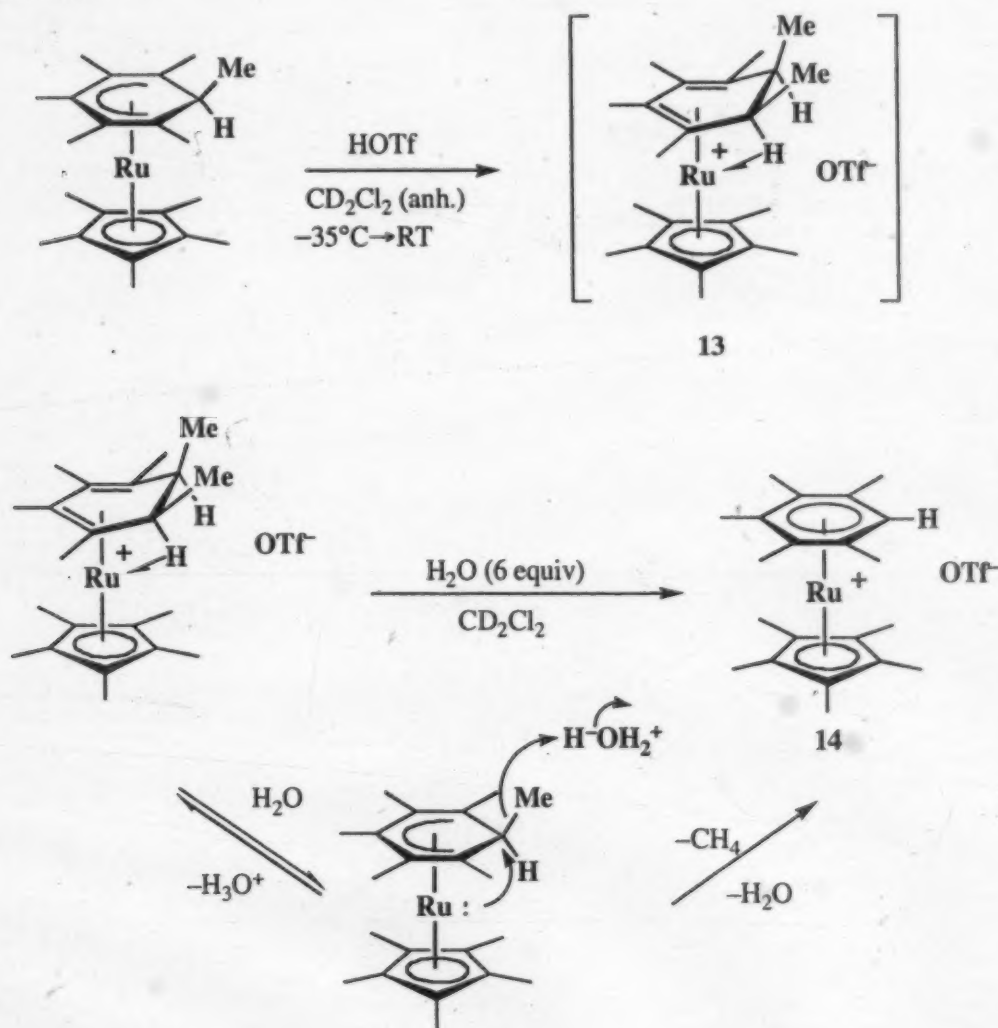
carbon activation occurs from the sterically hindered *endo* species which presents the methyl group proximal to the metal, while the *exo* isomer leads to the carbon-hydrogen activation product.

The idea that the *endo* species leads to carbon-carbon activation was subsequently established to be incorrect by Stryker and Older.¹² A series of protonation experiments involving ruthenium *endo* and *exo* substituted η^5 -cyclohexadienyl complexes was conducted. Upon protonation of 6-*endo*-hexamethylcyclohexadienyl complex in wet solvent, no carbon-carbon activation occurred. Instead, the exclusive formation of the η^6 -hexamethylbenzene complex **10** is observed (eq. 6a). However, when the 6-*exo*-hexamethylcyclohexadienyl is placed under the same conditions, methane and the η^6 -pentamethylbenzene complex **12** are formed (eq. 6b). It thus appears doubtful that carbon-carbon activation involving dealkylation to form an aromatic ring involves an *endo* transition state.



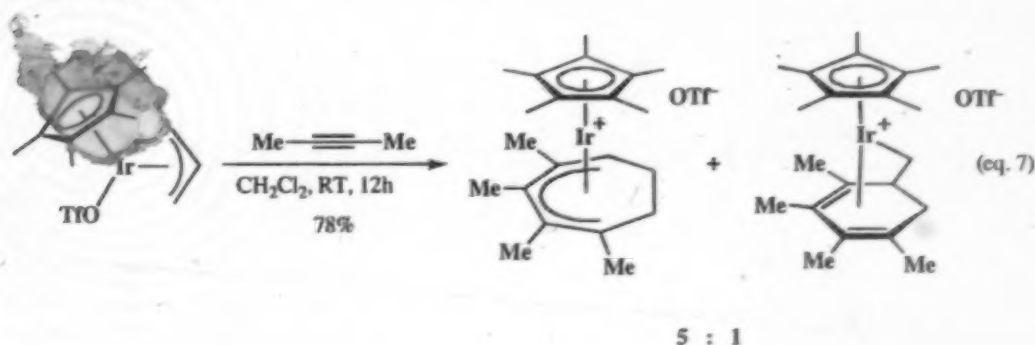
A mechanism for β -methyl elimination in the ruthenium chemistry was proposed by Stryker and Older (scheme 2).¹² Upon initial protonation under strictly anhydrous conditions, complex **13** is formed. This stable intermediate has been isolated and characterized by ^1H NMR spectroscopy. Upon treatment with a Lewis base (e.g., water), the carbon-carbon activation product **14** is obtained in near quantitative yield.

Scheme 2



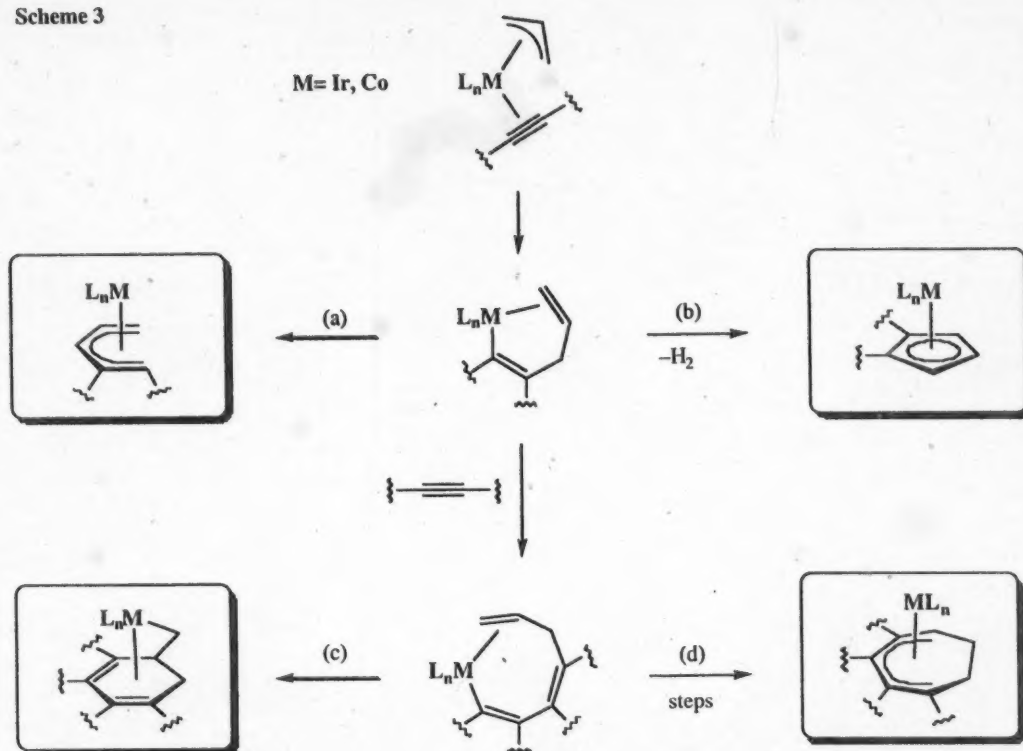
II. Allyl/alkyne[3+2+2] cycloaddition and cyclopentenyl/alkyne [5+2] ring expansion reactions.

Seven membered ring formation is a topic of great interest to synthetic organic chemists. This is particularly true in the pharmaceutical industry, since rings of this size remain somewhat difficult to construct. One novel pathway to seven-membered rings was first developed by Stryker and Schweibert.¹³ The reaction involves an iridium-mediated [3+2+2] allyl/alkyne coupling and cyclization (eq. 7). Further study by Stryker, *et al.*, showed that similar reactions could be achieved using analogous but much less expensive cobalt complexes.¹⁴



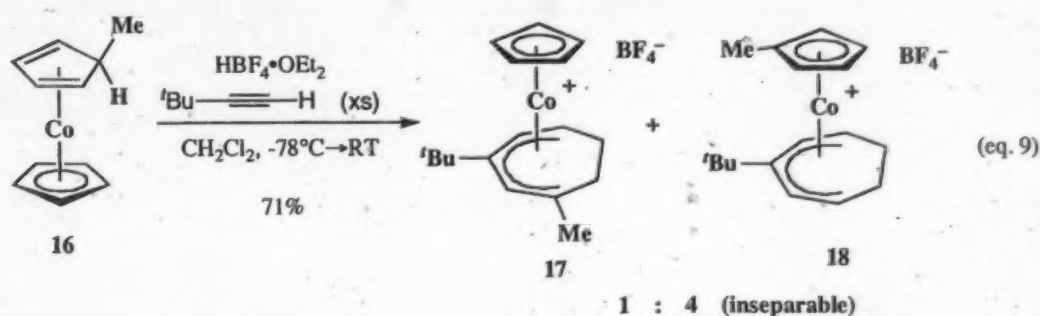
The fundamental pathway leading to seven-membered ring formation was suggested to be the one shown in Scheme 3 (path d). Alkyne insertion occurs twice, followed by a regioselective ring closure. As shown in Scheme 3, seven-membered rings are not the only possible product from such a pathway. Other potential products include open chain pentenyl, cyclopentadienyl, and methanocyclohexadiene systems, all preceded from reactions of other allylmetal complexes.

Scheme 3

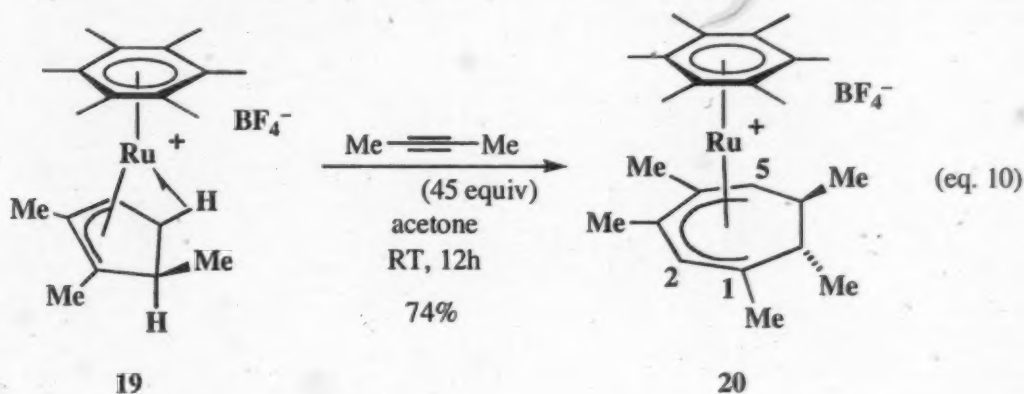


A particularly interesting and surprising result was obtained for cyclizations using 2-butyne mediated by (pentamethylcyclopentadienyl)cobalt(crotyl)(triflate). The positions of the methyl groups in the final cycloheptadienyl product **15** (eq. 8) are inconsistent with the pathway outlined in Scheme 2. More importantly, the unsubstituted carbons apparently originating from the allyl ligand are no longer contiguous, implying some sort of carbon-carbon bond cleavage. Two different carbon-carbon bond activation processes can be envisioned to explain this anomalous result. Either the methyl groups migrate specifically on the ring system or a carbon-carbon bond activation involving the original allyl carbons must be operating.^{14,16,17}

To provide further evidence in support of the proposed mechanism, Dzwiniel treated a cyclopentenyl cobalt complex, generated *in situ* by protonation of a cyclopentadiene complex **16**, with 2-butyne. This cobalt complex indeed gives seven-membered rings **17** and **18**, consistent with the proposed mechanism (eq. 9).^{14,17}



The cyclopentenyl/alkyne [5+2] ring expansion reactions are not limited to cobalt systems. Older¹⁸ observed similar chemistry on one ruthenium template. The agostic ruthenium arene complex **19** was treated with excess 2-butyne to furnish a new seven-membered ring product **20**, closely related to the previous cobalt complexes (eq. 10).¹⁸

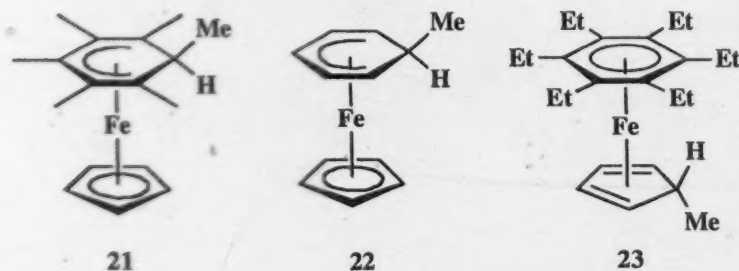


III. Project Goals.

Iron is the most abundant transition metal in the earth's crust. This makes iron an attractive transition metal for organometallic chemistry, both for its availability and low cost. However, the advantages do come at a price. First row transition metals have a much smaller ionic radius, creating steric issues at the metal, which leave much smaller spaces in which chemistry can take place. First row transition metals also resist conversion to higher oxidation states, resulting in a poor ability to insert into carbon-carbon bonds.

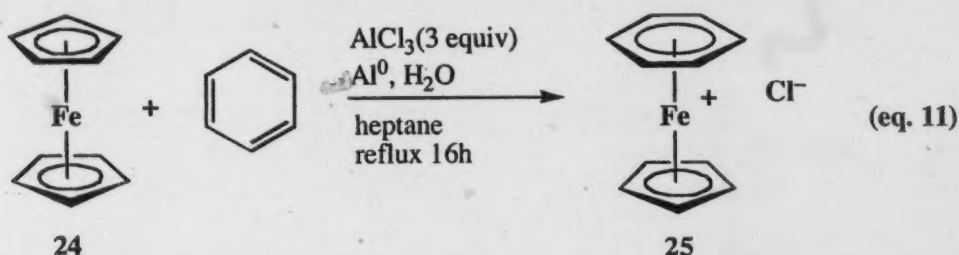
The objective of this investigation is to mimic using iron the aforementioned ruthenium carbon-carbon bond activation and allyl/alkyne cycloaddition chemistry. Using the iron templates developed by Pauson, Kaund, we hoped that (η^5 -hexadienyl)(Cp)Fe complexes **21** and **22** would be suitable to accomplish iron-based β -alkyl elimination reactions.¹⁸ These same complexes could also be used as templates for the cyclopentenyl/alkyne cycloaddition chemistry. A third candidate for the cyclopentenyl/alkyne cycloaddition chemistry could be complex **23** developed by Astruc.¹⁹

Figure 1. Target iron complexes for carbon-carbon activation and cyclopentenyl/alkyne cycloadditions chemistry



Chapter 1.2 Results and Discussion: Carbon-Carbon Bond Activation with Iron

Ferrocene is an eighteen-electron iron(II) sandwich compound, stable both to air and to water, and is thus an attractive, if unreactive, starting point for organoiron chemistry. Nesmeyanov, *et al.*, showed that strong Lewis acids cleave the bonds between iron and one of the cyclopentadienyl ligands in ferrocene.²⁰ If this is done in the presence of benzene or another aromatic ring compound, the corresponding η^6 -(arene)cyclopentadienyliron(II) cations **25** are formed (eq. 11).²⁰ η^6 -Arene (cyclopentadienyl) iron cations have been extensively studied and reviewed.¹⁹



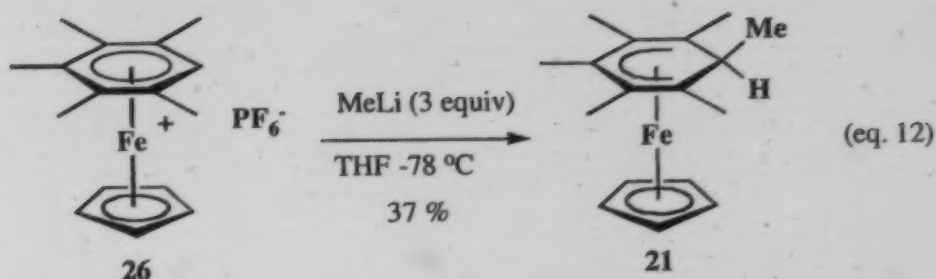
Aluminum is added to these reactions in order to prevent oxidation of ferrocene to ferrocenium. The function of water in these reactions is not quite clear, although its presence is required for high overall yields. One possible explanation is that in the presence of aluminum chloride, the water leads to HCl formation, which can then aid in the displacement of the cyclopentadienyl ring. This reactivity is not limited to the parent complex, but also works with substituted ferrocenes, such as 1,1'-dimethylferrocene. For isolation, these new compounds are normally converted into either the PF_6^- or BF_4^- salts, which are generally more crystalline and less sensitive to air and moisture. Using these conditions we were able to synthesize all of our required precursors in yields comparable to those published in the literature (*vide infra*). Only in the reaction between hexaethylbenzene and ferrocene were experimental difficulties encountered. Elevated

reaction temperatures led to ethyl loss from the aromatic ring. This problem was observed and investigated by Astruc: ethyl loss only occurs after the hexaethylbenzene is coordinated to iron.¹⁹ This fact is evidence that the carbon-carbon bond activation chemistry we hoped to demonstrate could indeed work.

I. Synthesis of the neutral iron templates.

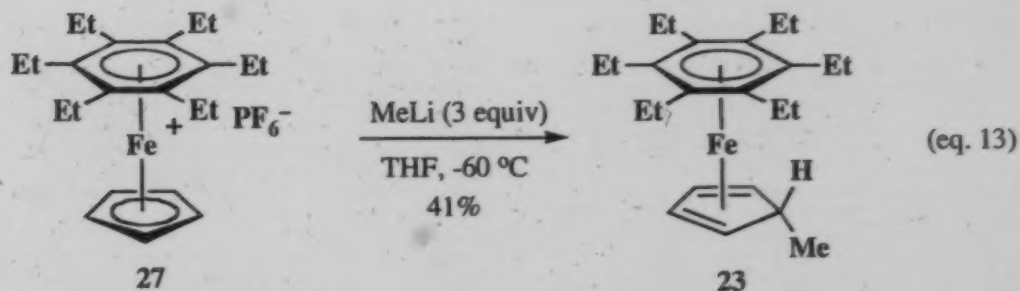
Arenecyclopentadienyliron(II) cations were of great interest to Pauson and Khand, who demonstrated that hydride reagents add selectively to the *exo* face of the arene ring to furnish neutral η^5 -hexadienyl(cyclopentadienyl)iron(II) species.²¹ This same reactivity pattern was also observed for alkyllithium reagents, which thus generate *exo* alkyl-substituted η^5 -hexadienyl ring complexes.¹⁸

Pauson and Khand first made $(\text{Cp})\text{Fe}(\eta^5\text{-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl})$ by addition of MeLi to $\text{CpFe}(\text{pentamethylbenzene})^+\text{PF}_6^-$, followed by an aqueous work-up and chromatography. Duplicating this procedure $\text{CpFe}(\eta^5\text{-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl})$ **21** was indeed obtained (eq. 12). However, the signals in ^1H NMR spectrum of the product was slightly broadened, indicating the presence of a paramagnetic impurity. In the hopes of obtaining a cleaner sample, we employed an anhydrous, anaerobic workup. Trituration with pentane, alumina chromatography in the dry box, and recrystallization furnished deep red crystals. The yield, though slightly lower than that obtained in the published procedure, gave rise to a sharper ^1H NMR spectrum. This new workup thus provides a more attractive pathway to obtaining clean product from methyl addition to $\text{CpFe}^+(\text{arene})$ complexes.



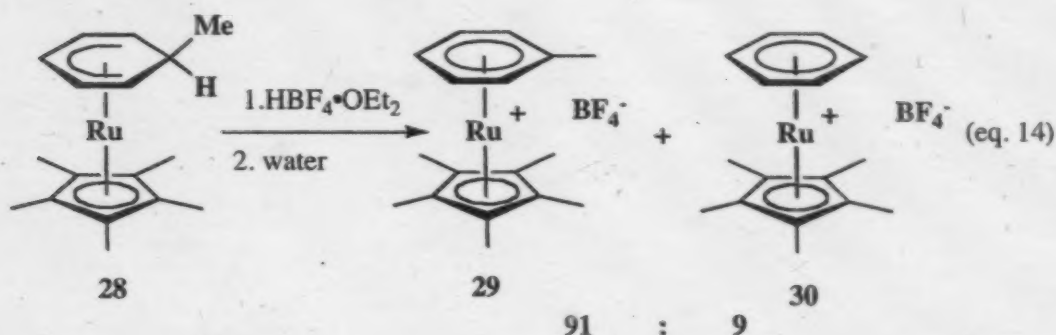
A notable exception to the above reactivity pattern occurs in the case of a fully substituted aromatic ring such as the hexamethylbenzene,¹⁸ or hexaethylbenzene complex 27.¹⁹ When MeLi is added to either complex, methyl attack occurs on the *exo* face of the cyclopentadienyl ligand, furnishing the neutral methylcyclopentadiene iron product 23 as illustrated (eq. 13).

In our hands, the conditions reported by Astruc for this reaction ($-40\text{ }^\circ\text{C}$, THF)¹⁹ failed to yield clean product. In hopes of obtaining a cleaner product, lower reaction temperatures were used ($< -40\text{ }^\circ\text{C}$), but with little improvement. Switching to 1,2-dimethoxyethane as a solvent also proved to be unsuccessful. The cleanest product was obtained from THF at $-60\text{ }^\circ\text{C}$ (eq. 13). The impurity in our material is manifested in the ^1H NMR spectral data as a series of multiplets with chemical shifts similar to the ethyl groups of the hexaethylbenzene ligand. Because of this, we believe that the minor impurity is likely due to methyl addition to the *exo* face of the hexamethylbenzene ligand.

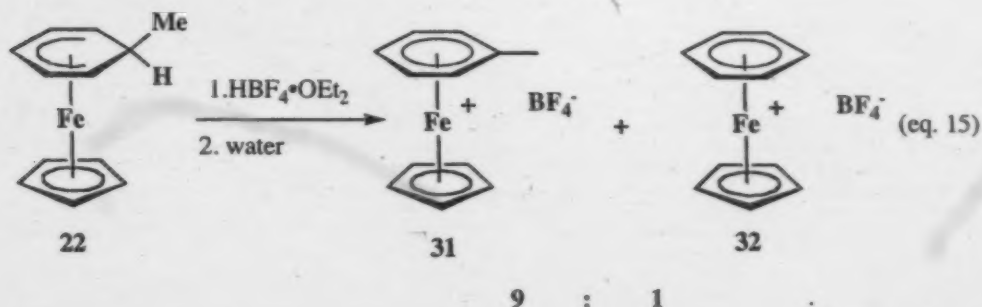


II. Protic acid addition to neutral iron sandwich templates

The first iron complex evaluated for carbon-carbon activation via protonolysis was the *exo*-methylcyclohexadienyl complex **22** (eq. 15). Older synthesized the analogous ruthenium complex **28** in order to investigate the intermediates that Itoh and Chaudret had proposed for the carbon-carbon activation product observed in their chemistry (Scheme 1, pg 4). Upon addition of $\text{HBF}_4 \cdot \text{OEt}_2$ followed by water to ruthenium complex **28**, complexes **29** and **30** were obtained in a ratio of 91 to 9 (eq. 14). This small amount of carbon-carbon activation product **30** obtained was similar to that obtained by Itoh¹¹ and Chaudret.¹⁰

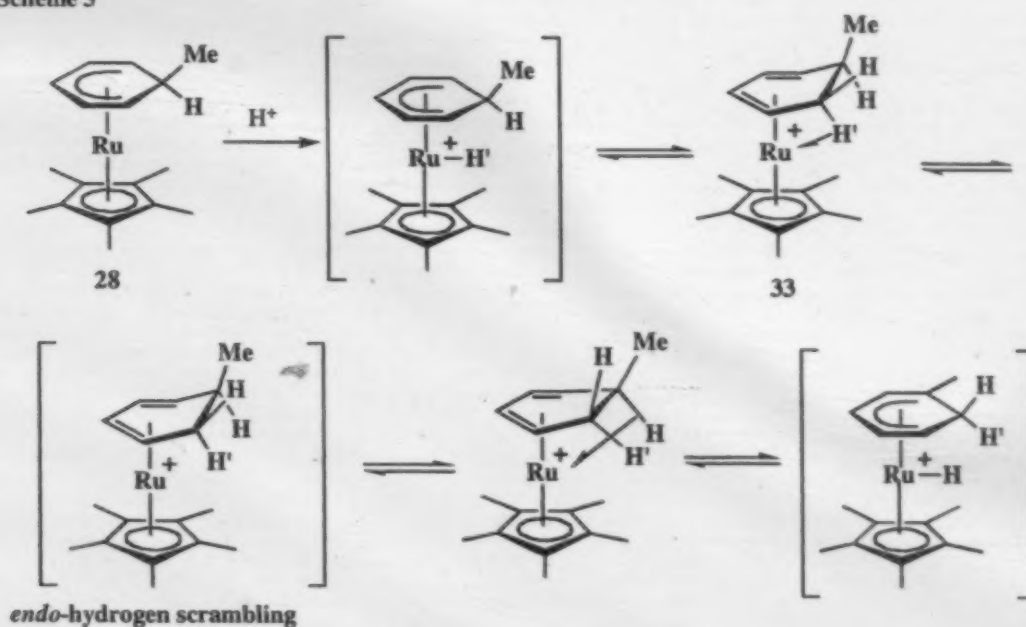


When $\text{HBF}_4 \cdot \text{OEt}_2$ was added to iron *exo*-methylcyclohexadienyl complex **22**, analogous products were obtained in a ratio of 9 to 1 in favor of the hydrogen loss product (eq. 15), which is almost identical to the ratio observed by Older in the corresponding ruthenium chemistry.



In order to explain the loss of hydrogen without use of the *endo*-methylcyclohexadienyl intermediate proposed by Itoh and Chaudret, Older theorized that the hydrogen loss product was due to an initial formation of an agostic species 33 which could undergo rapid hydrogen exchange with other *endo* hydrogens. This would lead to a scrambling of the methyl group into different positions on the cyclohexadienyl ring. As of consequence of the scrambling, *exo*-hydrogens and the *exo*-methyl group would then become available for protic abstraction (Scheme 5). Such fluxionality was well-characterized using the analogous hexamethyl ruthenium system.¹² This same argument can be used in the iron template to explain hydrogen loss.

Scheme 5

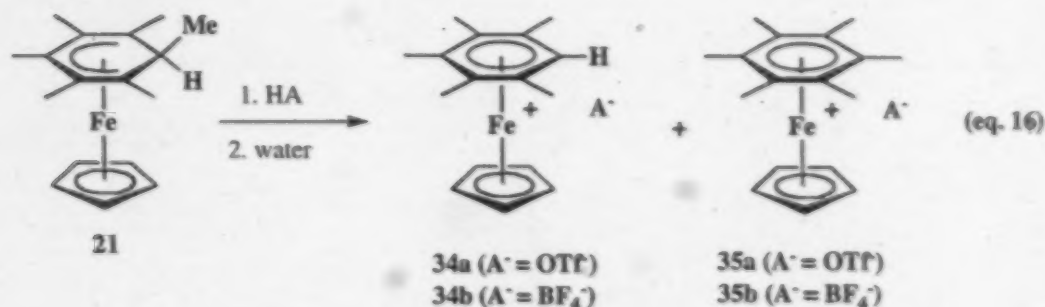


One disappointing aspect of the results obtained from the iron template was that even though carbon-carbon activation clearly occurred, the overall yield of both products was very low (~10%). Most of the product appeared to result from loss of the toluene ligand as free arene, along with some uncharacterized paramagnetic iron by-products.

The next system investigated for dealkylation was the $(C_5H_5)Fe(\eta^5-1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadienyl})$ complex **21**. A series of protonation experiments was performed under conditions which included varying the temperature, solvent and acid used. After addition of the acid, the mixtures were treated with five equivalents of water (eq. 16) (Tables 1.1 and 1.2). In all cases, methyl loss occurred in preference to hydrogen loss. However the yields were modest at best, with the highest isolated yield of 56% returned from reaction in THF at -60°C (Table 1.1).

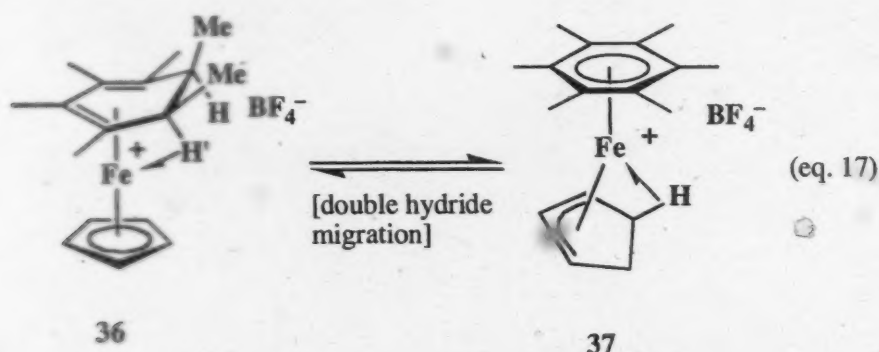
Table 1.1: Reactions of $(C_5H_5)Fe(\eta^5-1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadienyl})$ with $HB\dot{F}_4$

Solvent	Temperature	Yield of methyl Loss product	Yield of hydrogen Loss product	Ratio of Methyl loss to Hydrogen loss
CD_2Cl_2	-60°C	17.2%	3.4%	83:17
CD_2Cl_2	Room temp.	18.0%	4.2%	81:19
Acetone	-60°C	37.2%	16.7%	69:21
Acetone	Room temp.	35.3%	13.8%	72:18
THF	-60°C	42.6%	14.2%	75:25
THF	Room temp.	31.8%	14.3%	69:21



By comparison, Older was able to obtain near quantitative yields from dealkylation of $(C_5Me_5)Ru(\eta^5-1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadienyl})$ **11** (eq. 6b p. 5).¹² A plausible explanation for the increase in hydrogen loss is most likely due to the change from Cp^+ ligand to the Cp ligand. In the Cp case, hydrogen atoms can readily

migrate down from the six membered ring much more easily than in the case of the Cp^+ ligand. If a hydrogen does migrate, it would position a hydrogen atom on an *exo* position on the Cp ligand, which would be available for abstraction by protic acid. Attempts were made to prove this hypothesis by synthesis of the Cp^+ iron analogue; however, the desired complex was never obtained cleanly.



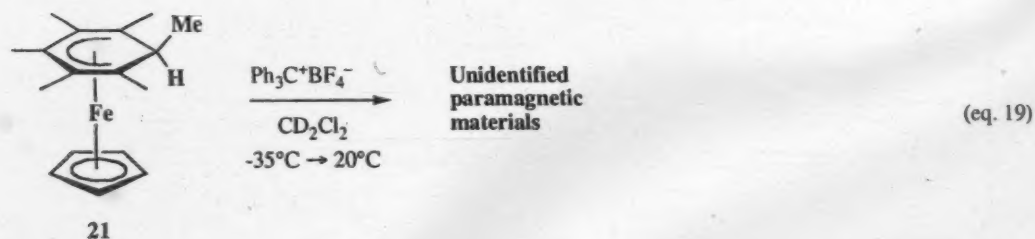
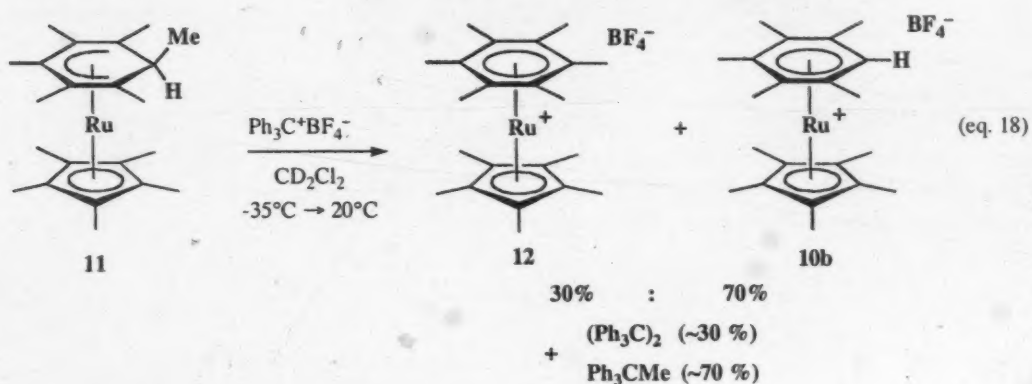
Modification of the experimental conditions appears to have a definite effect on the outcome of these reactions. First, the chemical yields obtained for overall product formation, be it hydrogen or methyl loss, were greater in polar oxygenated solvents. A possible explanation for this is that when acid is first injected into the NMR tube, the solvent would be protonated kinetically. It is this protonated solvent that is actually involved in protonation of the iron complex. In the case of dichloromethane the HBF_4 etherate would be the active acid.

Table 1.2: Reactions of $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl})$ with Triflic acid.

Solvent	Temperature	Yield of methyl Loss	Yield of hydrogen loss	Percent methyl loss to hydrogen loss
CD_2Cl_2	-60°C	26.5%	9.8%	73:27
CD_2Cl_2	Room temp	27.9%	10.3%	72:28

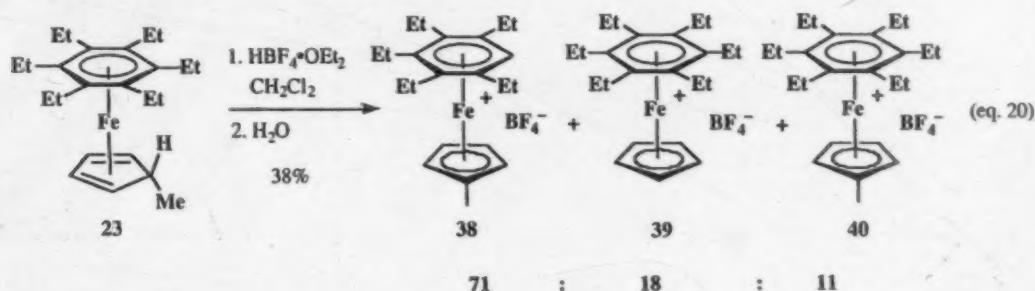
The specific acid has an effect on the yield obtained during these reactions. In dichloromethane, the use of triflic acid afforded a greater yield than that obtained from tetrafluoroboric acid (Table 2). It may be that a competing pathway to protonation is oxidation of iron by the active acid. The hypothetical iron (III) species could then somehow further react to lose the arene ring. Protic acid oxidation of iron sandwich compounds is known in the literature, H_2SO_4 , HBF_4 , and HPF_6 have all been used in the production of Cp_2Fe^+ .²² The decrease in yield in the dichloromethane solvent could also be a result of the less Lewis basic environment of the solvent.

Whichever pathway is leading to oxidation of iron, it appears that the iron complexes are much more susceptible to oxidation under these conditions than the ruthenium complexes. This difference was also apparent upon the addition of trityl cation to the ruthenium complex **11** and iron complex **21** (eq. 18 and 19).¹² In the iron



chemistry, addition of trityl cation leads to formation of uncharacterized paramagnetic material, whereas in the ruthenium chemistry, a mixture of hydrogen and methyl loss products were obtained nearly quantitatively, with only the hydrogen loss product arising from one electron oxidation. This is deduced from the ration of $(\text{Ph}_3\text{C})_2$ to Ph_3CMe formed.

The most interesting results obtained for carbon-carbon bond activation occurred using the (hexaethylbenzene) $\text{Fe}(\eta^4\text{-5}(\text{exo})\text{-methylcyclopentadienyl})$ complex **23** (eq. 20). When this complex was successively treated with $\text{HBF}_4 \cdot \text{OEt}_2$ and water, two distinct carbon-carbon activations products were present. The expected methyl loss from the cyclopentadienyl ligand to furnish **39** did occur, but only in a small amount relative to the major carbon-carbon activation product, which was the loss of one of the ethyl groups from the hexaethylbenzene ligand to form **38**. The third product from this reaction is complex **40**, resulting from hydrogen loss. Both **38** and **40** are most likely formed by the *endo* hydrogen of the methylcyclopentadienyl ring migrating to the iron, either completely or as an agostic hydrogen. From this position it could move up to the hexaethylbenzene ligand to give de-ethylation product **38**, or back down to another position on the cyclopentadienyl ring, thus placing a hydrogen in an *exo* position, making it available for abstraction to give **40**.



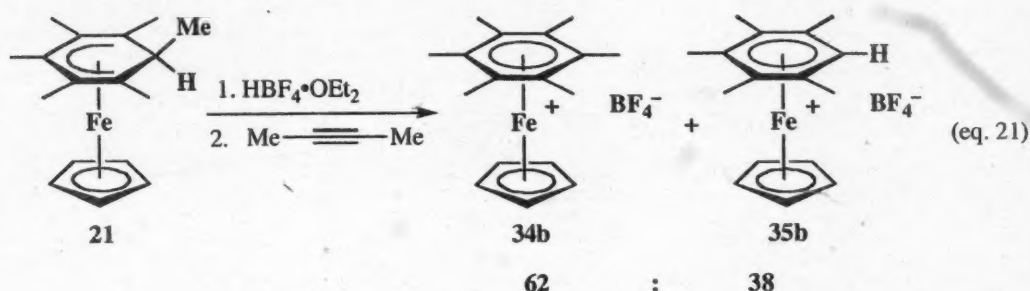
The combined chemical yield for the three different products was low (38%). Again, most of the starting material ends up as a mixture of free arene and some paramagnetic iron compound.

Although we were able to achieve carbon-carbon activation in all cases, the use of iron in the form of these templates does not seem to be a viable option for synthetic organic chemistry. It appears that the arene ligands are not bonded strongly enough to iron, resulting in poor overall yields for all the various carbon-carbon bond reactions we evaluated.

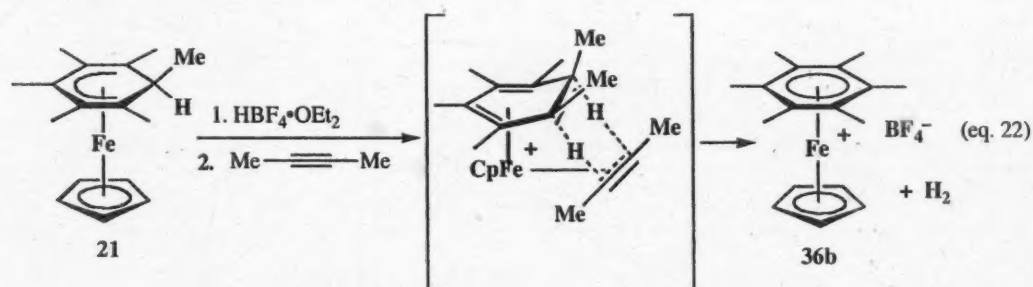
II. Alkyne addition chemistry

Older and Dzwiniel^{12,16} were able to obtain seven-membered rings using ruthenium and cobalt templates, respectively, by a [5+2] pathway involving cleavage of cyclopentenyl carbon-carbon bond and alkyne insertion (eq. 9 and 10, p. 10). In order to duplicate this reaction pathway in iron chemistry we first considered the reactions of $(C_5H_5)Fe(\eta^5-1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadienyl})$ complex **21**. The complex was first protonated with HBF_4 etherate at low temperature, then treated with various alkynes. Acetylene, 2-butyne and diphenylacetylene all proved unsuccessful in generating any [5+2] insertion product. In hopes of obtaining at least some carbon-carbon bond activation product, modification of the solvent and reaction temperature were tried, to no avail. Varying the amount of alkyne from 5 to 100 equivalents also proved ineffective. Most of the material seems to be lost as free arene, producing some unknown paramagnetic product. In one treatment of **36** with 2-butyne, the small amount of non-paramagnetic product obtained was characterized by ^1H NMR spectroscopy. Two products were

identified and confirmed by comparison with independently synthesized complexes. The major product arises from hydrogen loss to form **35b** and the minor product **34b** was the result of loss of the *exo*-methyl substituent (eq. 21).

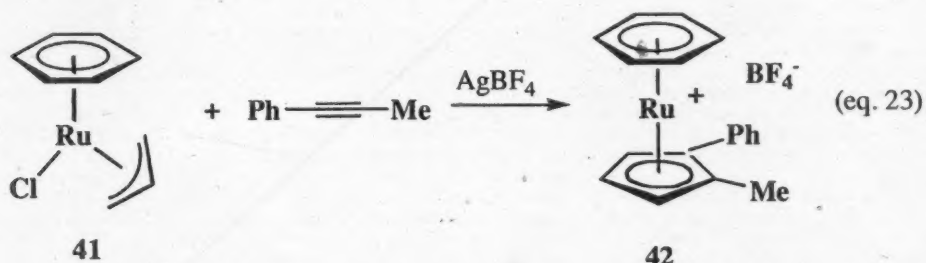


The mechanistic pathway by which hydrogen was lost was not investigated, but at least two plausible pathways can be suggested. One possibility is an ionic reaction in which the alkyne is first protonated and then later accepts a hydride from the iron complex. A second, more interesting possibility, involves a concerted hydrogenation reaction involving a 6-membered ring transition state, in which the alkyne is coordinated to the iron center. The driving force for this reaction could be the formation of the fully coordinated aromatic ring (eq. 22).

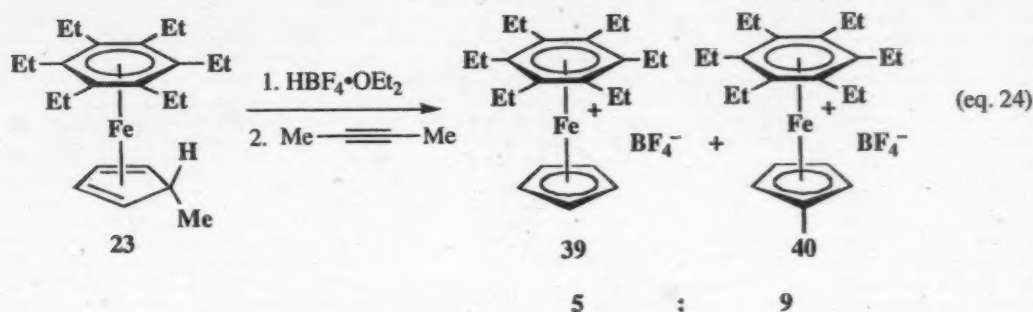


There is literature precedent for the formation of alkene side products from similar allyl/alkyne coupling reactions. Rubezhov reported that during a [3+2] allyl/alkyne coupling of tolane and the ruthenium complex **41**, the expected cyclopentadienyl ring product **42** was obtained (eq. 23).²³ In order to determine in what

form the two hydrogens are lost during product formation the examined the reaction mixture. Rubeshov found the presence of both H₂ gas, as well as stilbene, but no isopropyl alcohol, which would result from reduction of the acetone solvent, was observed. The reaction mixtures from our reactions were never investigated for the presence of *cis*-alkenes.



After the failure of the hexamethylbenzene iron complex **21** to furnish any seven-membered ring product, we turned to the investigation the hexaethylbenzene iron complex **23**. This compound has the advantage that one of the hydrogens needed for the [5+2] ring expansion to occur is already located on the Cp ring. When (hexaethylbenzene)Fe(η^4 -5-(exo)-methylcyclopentadienyl) **23** was treated with HBF₄•OEt₂ and alkyne (acetylene, diphenylacetylene, or 2-butyne), no [5+2] product was observed. The reaction resulted mostly in the formation of free arene and unidentified paramagnetic iron products, just as in the hexamethylcyclohexadienyl ligand complex. The products obtained in low yield from reactions with 2-butyne, were determined to be those products resulting from both hydrogen and methyl loss from the cyclopentadienyl ring (eq. 24). The hydrogen loss product **39** was obtained in greater yield than the methyl loss product **40** (5 : 9). This ratio was determined by ¹H NMR spectroscopy and the products identified by comparison with independently synthesized **39** and **40**.



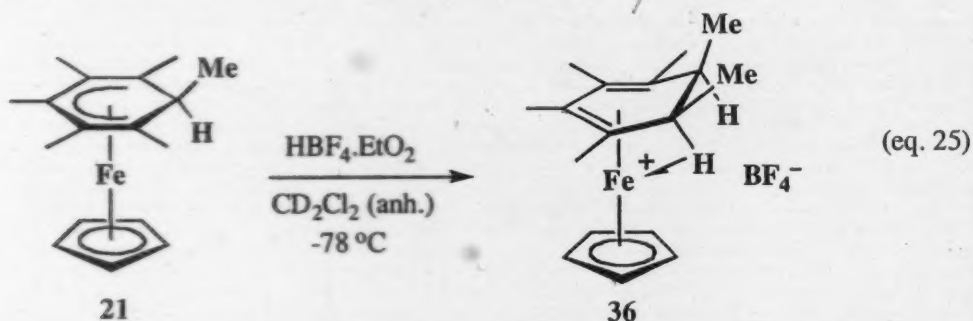
Attempts were also made to observe ring expansion using the $(C_5H_5)Fe(\eta^5-6(exo)-methylcyclohexadienyl)$ template **22** but as in the other systems, no apparent cyclization occurred when either 2-butyne or acetylene were used in the protonation procedure.

IV. Variable temperature experiments

In order to help explain the low yields in both series and the lack of cyclization products in the alkyne addition chemistry, variable temperature NMR experiments were undertaken on reaction mixtures obtained from protonation. The experiments were performed in dried, degassed deuterated dichloromethane in the hope of observing and characterizing the protonated intermediate.

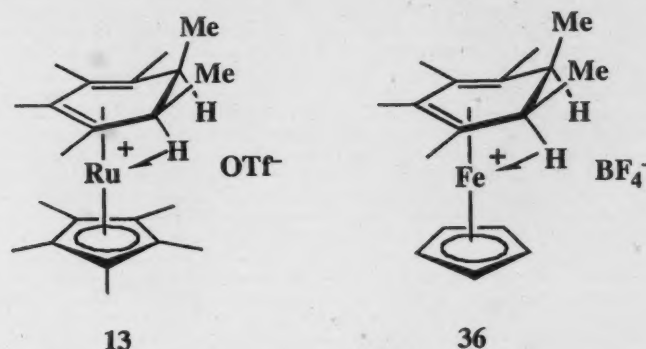
Our first experiments were done on the $(C_5H_5)Fe(\eta^5-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl)$ complex **21**. Upon treatment with $HBF_4 \cdot OEt_2$ at low temperature the solution changed from orange to dark red immediately. This instantaneous change was also observed by Older upon treatment of the analogous Cp^* ruthenium complex with acid.¹² We identify the new compound formed as a novel cationic agostic iron species, $[(C_5H_5)Fe(\eta^4-1,2,3,4,5(exo),6(exo)-hexamethylcyclohexa-1,3-diene)]^+BF_4^-$ **36** by NMR spectroscopy (eq. 25). All relevant resonances are present, though somewhat broadened, in the ^1H NMR spectra. There is no significant change in

peak intensities or positions when the temperature is raised from $-100\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$. Both ^1H and ^{13}C NMR spectra appeared reasonably clean. This agostic species was stable at $-60\text{ }^{\circ}\text{C}$ for 24 hours, with only slight additional broadening of the spectrum. However, if left overnight at room temperature, the spectrum becomes very broad, indicating a degradation to some unidentified paramagnetic material.



Comparison of the NMR spectroscopic data of the iron complex with that of $(\text{C}_5\text{Me}_5)\text{Ru}(\eta^4\text{-}1,2,3,4,5(\text{exo}),6(\text{exo})\text{-hexamethylcyclohexa-}1,3\text{-diene})]^+\text{BF}_4^-$ **13** (p. 6) reveals a few interesting points. Both complexes exhibit a highly shielded proton, indicative of an agostic hydrogen. However, the agostic hydrogen in iron complex **36** is much further upfield at $\delta -10.66$ ppm compared to $\delta -5.73$ ppm for the corresponding hydrogen in ruthenium complex **13**. Each spectrum contains one upfield methyl group, the iron complex at $\delta -0.2$ ppm and the ruthenium analogue at $\delta 0.33$ ppm. Interestingly, in the iron complex there are three more methyl signals ($\delta 2.82$, $\delta 1.99$, and $\delta 1.53$) integrating 1 : 2 : 2 respectively, but in the ruthenium complex only two other methyl signals are observed ($\delta 2.37$ ppm and $\delta 1.79$ ppm) integrating 1:4 respectively. Both compounds give rise to a distinct signal for the non-agostic *endo* hydrogen, at $\delta 1.76$ ppm for the iron case and $\delta 2.59$ ppm for the ruthenium complex.

Figure 1.2 Structures for NMR spectroscopic comparison



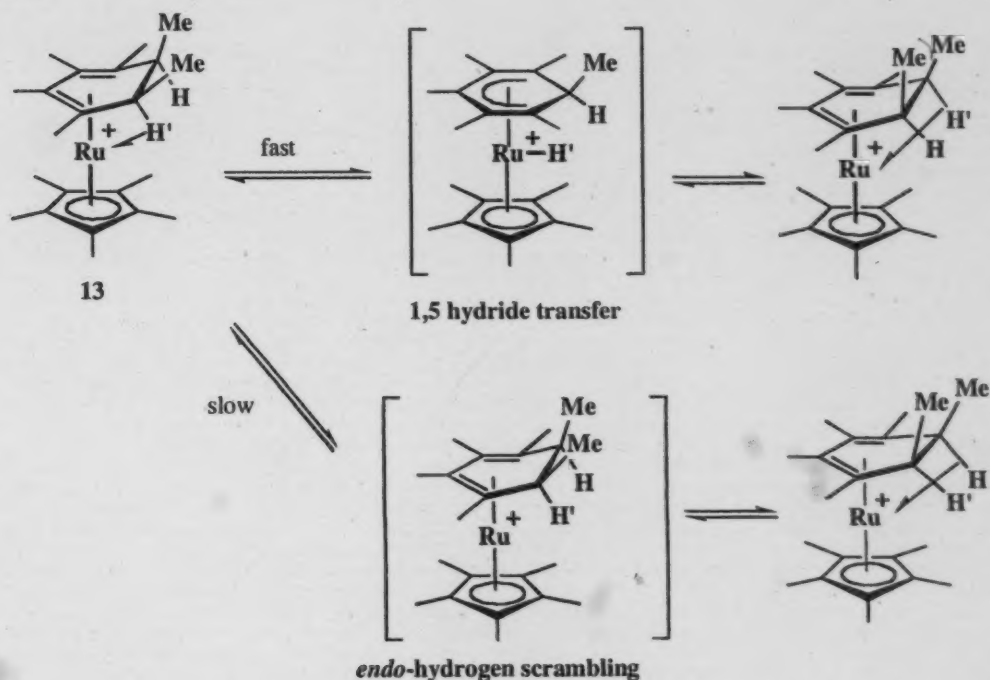
Agostic hydrogen complexes are quite common in organometallic chemistry, although iron examples are somewhat less common. One such iron complex, $[\text{Fe}(\text{P}(\text{OMe})_3)_3(\eta^3\text{-cyclooctenyl})]^+\text{BF}_4^-$,²⁴ exhibits an upfield agostic hydrogen signal at δ -6.54 in the ^1H NMR spectrum. This is not as upfield shifted as that in complex 36; however, the ligands on the two systems are vastly different and the hydrogen in complex 36 may be more perturbed towards the iron. The upfield shift due to substantial iron hydride character of the bond seems reasonable. One example of a purely iron hydride ^1H NMR resonance has reported by Green and Wong²⁵ for the hydride in iron complex, $[\text{FeH}(\text{C}_5\text{Me}_5)(\text{PMe}_3)(\eta^2\text{-C}_2\text{H}_4)]$. This resonance is located at δ -11.77 ppm.

Evidence that the signal at δ -10.66 is due to an agostic hydrogen and not a classical iron hydride is found in the ^1H -coupled ^{13}C NMR spectrum. The doublet at δ 42.31 ppm has a $^1J_{\text{CH}}$ coupling constant of just 32 Hz. This is a very small coupling constant, even for an agostic hydrogen, which again suggests that the hydrogen bonding is more perturbed towards the iron than toward carbon.

Application of decoupling pulses on the iron and ruthenium complexes gave parallel spin saturation transfer results in the ^1H NMR spectra. When the upfield signal

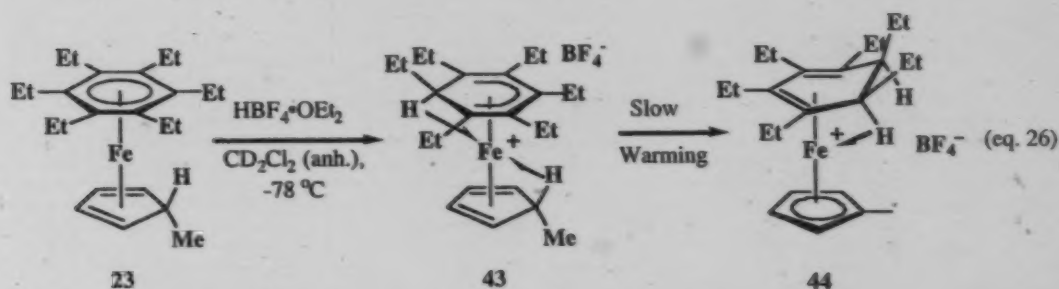
attributed to the agostic hydrogen is irradiated, the signal attributed to the adjacent *endo* hydrogen disappears in the spectra of both complexes. If the signal attributed to the *exo*-methyl group is irradiated, all of the other methyl groups located on the six-membered ring decrease drastically in intensity in both **13** and **36**. Using this data for ruthenium along with deuterium labeling experiments, Older concluded that there were two separate fluxional processes occurring in the agostic complex **13**: facile 1,5-intraligand hydride transfer of the agostic hydride, and a slower scrambling of the two *endo* hydrogens (Scheme 6). In the ruthenium complex **13**, the slower *endo*-hydrogen scrambling was frozen out at $-80\text{ }^{\circ}\text{C}$. This was evident by the change in multiplicity and chemical shift for the hydrogen signal at $\delta\text{ }2.37\text{ ppm}$ and the methyl signal at $\delta\text{ }0.33\text{ ppm}$. At $-80\text{ }^{\circ}\text{C}$, a methyl doublet appeared at $\delta\text{ }0.22$ ($J = 6.5\text{ Hz}$) no longer a broad singlet, and the *endo* hydrogen moved slightly downfield to $\delta\text{ }2.53$ ($J = 6.6\text{ Hz}$). In the case of iron, no

Scheme 6



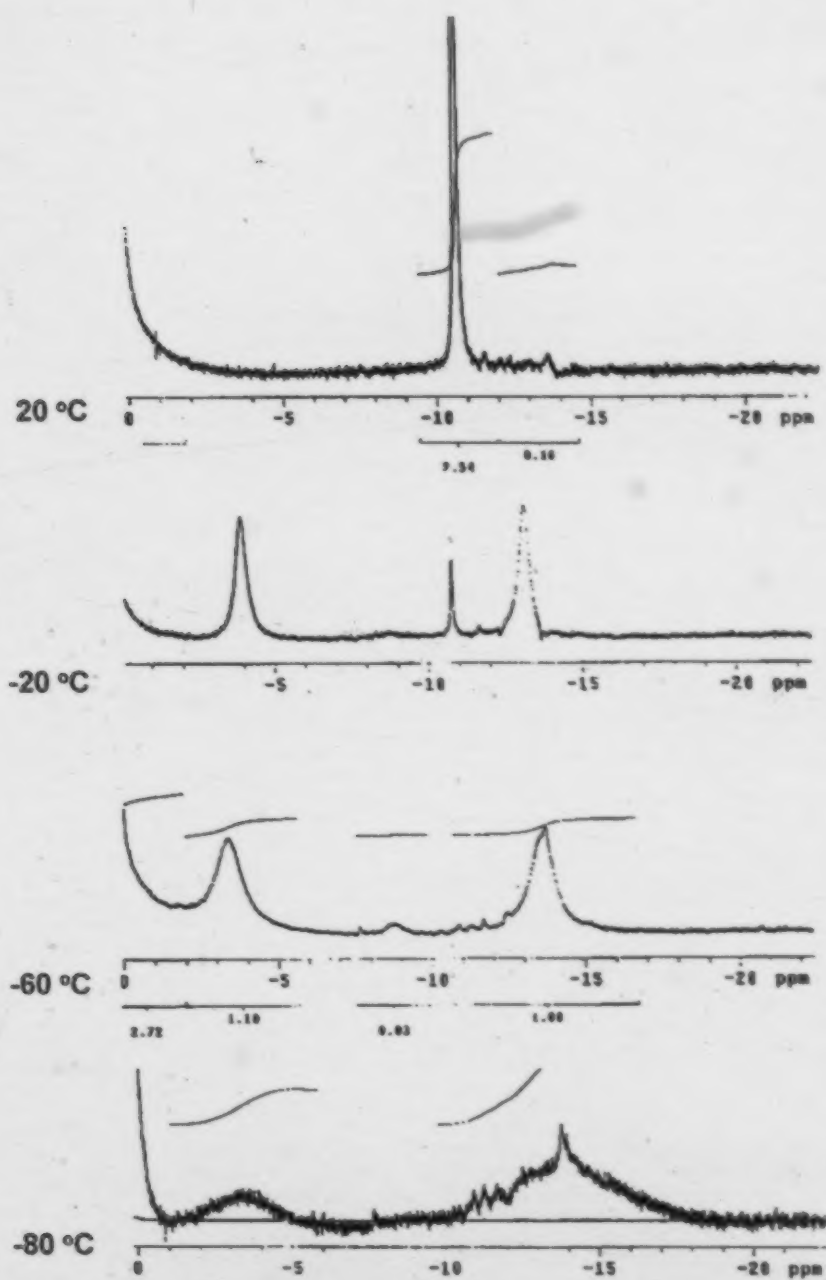
coupling is seen between the *endo* hydrogen and methyl group even at -100°C . This suggests that the rate of *endo*-hydrogen scrambling in complex **36** must be faster than in the ruthenium complex **13**.

Similar low temperature protonation experiments were also performed on (hexaethylbenzene)Fe(η^4 -5(*exo*)-methylcyclopentadienyl) **23** (eq. 26). Upon treatment of **23** with one equivalent of $\text{HBF}_4 \cdot \text{OEt}_2$ at -78°C the solution immediately darkened. Examination of the ^1H NMR spectrum recorded at -78°C revealed a somewhat unexpected result. Instead of the expected single upfield agostic signal, two vastly different upfield signals were found (Figure 1.3). The first was located slightly upfield at δ -3.6 and the second was much further upfield at δ -13.3. As the sample was slowly warmed, an even more interesting change was observed. At approximately -20°C , the two signals began to decrease in intensity, coinciding with the appearance of a third upfield signal at δ -10.7. This trend continued until at room temperature, only the signal at δ -10.7 remained. This process was not reversible, as cooling the sample back down to -78°C resulted in no reappearance of the original upfield signals.



We believe the spectral data seen at -78°C may be attributable to a novel cationic double agostic iron species $[(\eta^4$ -5(*exo*)-methylcyclopenta-1,3-diene)Fe(η^5 -1,2,3,4,5,6(*exo*)-hexaethylcyclohexa-1,3-dienyl)] $^+\text{BF}_4^-$ **43**. This assignment is based on

Figure 1.3 Variable temperature ^1H NMR data for protonation of complex 23.



the ^1H NMR spectrum obtained at -80°C and comparison with the spectral data obtained for compound **36**. In compound **36**, we established that the proton at δ -11.66 was due to an agostic C-H bond. Evidence for the agostic nature of this bond was indicated by the $^1J_{\text{CH}}$ of 30 Hz. Considering that the ^1H NMR spectrum of complex **43** reveals an even more shielded hydrogen resonance at δ -13.6, this suggest that this agostic hydrogen may be even more iron hydride-like in character than the agostic hydrogen in complex **36**. Hence, the signal at δ -3.6 would have to be due to an agostic C-H bond that contains a much less significant hydrogen-iron interaction.

As the temperature is increased, it appears that the hydrogen located on the cyclopentadiene ring migrates to the six-membered ring, forming the new cationic agostic complex $[(\text{MeCp})\text{Fe}(\eta^4\text{-}1,2,3,4,5(\text{exo}),6(\text{exo})\text{-hexaethylcyclohexa-1,3-diene})]^+\text{BF}_4^-$ **44**. The spectral data of **44** appears analogous to the data obtained for iron complex **36**, with the expected changes in moving from methyl groups to ethyl groups on the cyclohexadiene ring. The agostic hydrogen signals in both **36** and **44** have an almost identical chemical shifts of approximately δ -11.7. In the ^{13}C NMR spectrum the signal attributed to the carbon attached to the agostic hydrogen moves downfield from δ 42.31 in iron complex **36** to δ 52.6 in iron complex **44**. We were unfortunately unable to obtain $^1J_{\text{CH}}$ for the carbon at δ 52.6, although the signal does broaden significantly, and remains centered at δ 52.62 ranging from δ 53.0 to δ 52.3 with an approximate coupling constant of 60 Hz, measured by width at half the height.

It is clear from the variable temperature NMR data of both complexes that the problems associated with low yields in the carbon-carbon bond activation reactions do not occur upon initial protonation. In both complexes, the protonation appears clean and

the resultant product is stable at low temperatures. Therefore, the decomposition that accompanies the carbon-carbon activation must occur after the addition of the water and at higher temperature. In the alkyne insertion chemistry, it appears that the most thermodynamically stable intermediates contain cyclopentadienyl ligands, where the hydrogens have moved to the six-membered ring. In order for alkyne insertion to occur, the *endo* hydrogens on the cyclohexadiene fragment would need to migrate down to the cyclopentadienyl ring, an apparently unfavorable process. We have no concrete evidence to either prove or refute this hypothesis. However, steric interactions might also explain why alkyne insertion does not take place in the iron complexes investigated. There may simply not be enough room for an alkyne to fit between the two rings and bind to iron, which would be the required first step in alkyne insertion.

With the failure of the arene complexes to undergo clean carbon-carbon activation chemistry and [5+2] alkyne chemistry we considered the use of other ancillary ligands. 1,4,7-Trimethyl-1,4,7-triazacyclononane, like benzene, it is a six electron neutral ligand. However its bonding is fundamentally different, being a tridentate ligand that makes three dative bonds to the metal from the nitrogen lone pairs to the metal center. We conducted a few preliminary trials to induce trimethyl-1,4,7-triazacyclononane to exchange with the arene ligand, thus far without success.

1.3 Experimental Procedures

Reagents and Methods. All manipulations on air sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques, or in a Vacuum Atmospheres He-553-2 Dri-lab equipped with a Mo-41-1 inert gas purifier and a CD-882 Dri-Cold Freezer maintained at -35°C . Toluene, benzene, tetrahydrofuran, diethyl ether, hexane and pentane were distilled from sodium/benzophenone ketyl or sodium (potassium)/benzophenone ketyl. Reagent grade acetone was degassed and stored under nitrogen with no further purification. Dichloromethane and acetonitrile were distilled from calcium hydride and degassed. Acetylene was used without further purification. Unless stated otherwise, all reactions were carried out under a nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (^1H , 400 MHz; ^{13}C , 100 MHz), Bruker AM-360 (^1H , 360 MHz), Bruker AM-300 (^1H , 300 MHz; ^{13}C , 75 MHz) or a Varian Unity-Inova 300 (^1H , 300 MHz) spectrometer. High resolution mass spectra were obtained on a Kratos MS-50 spectrometer (electron impact ionization (EI)) and elemental analyses were performed by the University of Alberta Microanalysis Laboratories.

Further Notes on Spectroscopic Methods. Chemical shifts are reported relative to residual protiated solvent. In ^1H NMR spectral data, values of the coupling constants are either obtained directly from the spectrum, or extracted using standard homonuclear decoupling techniques. Although generally measured to ± 0.1 Hz, J values are self-consistent only to ± 1 Hz. GCOSY denotes the standard COSY experiment, acquired using field gradients. Data for the ^1H - ^1H COSY or GCOSY is presented such that correlations are listed only once. Values of $^1J_{\text{CH}}$ are obtained either directly from the

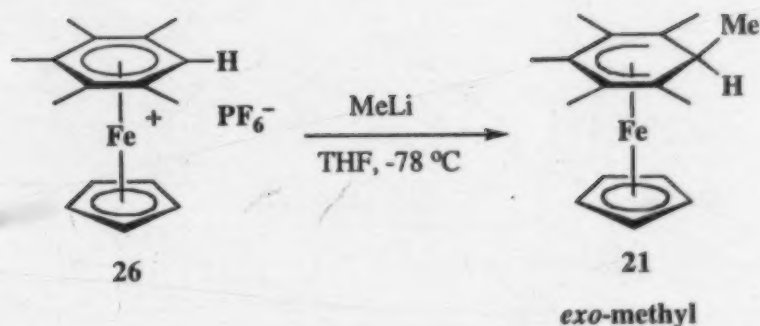
gated decoupled spectrum, or from the coupled HMQC spectrum. HMQC and HMBC spectra are recorded at the ^1H frequency.

The following compounds were prepared by published procedures:

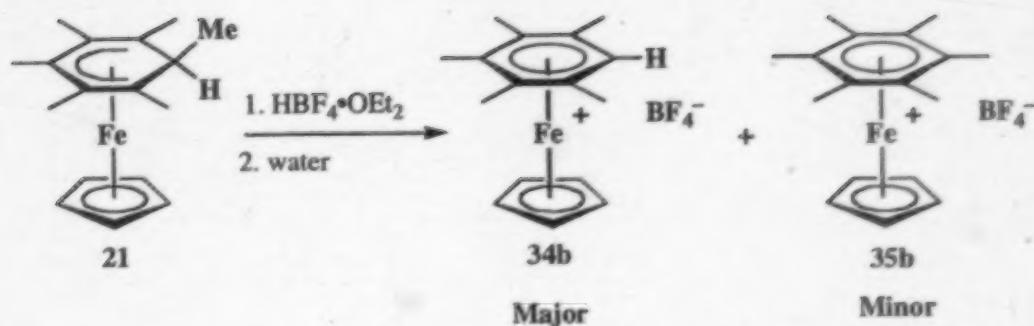
$[\text{CpFe}^+(\text{pentamethylbenzene})]^+ \text{PF}_6^-$ (**26**),²¹ pentamethylbenzene,²⁶

$[\text{CpFe}(\text{hexaethylbenzene})]^+ \text{PF}_6^-$,²⁷ Trimethyl-1,4,7-triazacyclononane, $[\text{CpFe}^+(\text{benzene})]^+ \text{PF}_6^-$.^{28,29,30}

Experimental



(C₅H₅)Fe(η⁵-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl) (**21**). This procedure is a modification of that initially reported by Pauson.¹⁸ In a Schlenk flask under nitrogen, [CpFe⁺(pentamethylbenzene)]⁺ PF₆⁻ (3.65 g, 8.81 mmol) was dissolved in THF (50 mL). The solution was cooled to -78 °C and MeLi (26.4 mmol, 1.4M) was added dropwise via syringe. The solution was then warmed to room temperature overnight. The following morning, the solvent was removed under reduced pressure, furnishing a dark red-brown residue, which was brought into the drybox for workup. The residue was triturated with pentane (3×20 mL) and the resulting pentane solution passed through small columns of celite and activity III neutral alumina. The pentane was then concentrated in vacuo to about 10 mL. The solution was then cooled slowly in a schlenk flask outside the box to -60°C to induce crystallization. After four hours the remaining pentane was removed via canula to yield deep red crystals of the known product **21** (0.93 g, 37%). Spectroscopic data for complex : ¹H NMR (300 MHz, C₆D₆) δ 3.70 (s, C₅H₅), 2.34 (s, 3H), 2.15 (q, *J* = 9.0 Hz, 1H), 1.76 (s, 6H), 1.59 (s, 6H), 0.07 (d, *J* = 9.0 Hz, 3H).



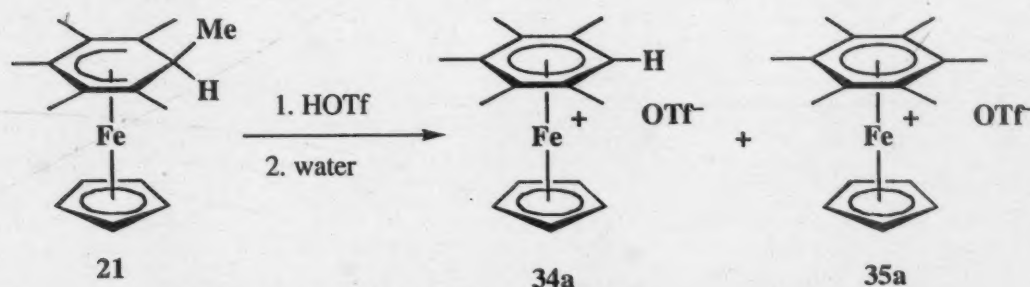
Reactions of (Cp)Fe(η^5 -1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl) with HBF₄.

In the dry box, (Cp)Fe(η^5 -1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl) complex **21** (83.3 mg, 0.293 mmol) was dissolved in THF (2 mL). The red solution was shaken, then transferred to an NMR tube, which was capped with a small rubber septum, wrapped with parafilm, and removed from the box. The solution was then cooled to -60°C , and HBF₄·OEt₂ etherate (39 μL , 0.284 mmol) was added via microsyringe. An immediate change was observed as the solution turned much darker. After 5 minutes, water (11.5 μL , 1.25 mmol) was added via microsyringe. The solution was shaken, returned to the -60°C bath, and allowed to warm slowly to room temperature overnight. Solvent was removed under reduced pressure, leaving a yellow powder, which was washed with small amounts of pentane and cold ether. The compound was then dissolved in acetone and passed through a small plug of celite to remove small amounts of insoluble material. Upon evaporation of the acetone, a mixture of the two known compounds, CpFe(pentamethylbenzene)⁺ PF₆⁻ (42.6%) and CpFe(hexamethylbenzene)⁺ PF₆⁻ (14.2%) was obtained. The product ratio and identities were determined by spectroscopic comparison with known literature compounds.

A range of reaction conditions was investigated, as detailed in Table 1.

Table 1: Reactions of $(C_5H_5)Fe(\eta^5-1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadienyl})$ with HBF_4^-

Solvent	Temperature	Yield of methyl loss product	Yield of hydrogen Loss product	Percent CC activation
CD_2Cl_2	$-60^\circ C$	17.2%	3.4%	83.5%
CD_2Cl_2	Room temp.	18.0%	4.2%	81.1%
Acetone	$-60^\circ C$	37.2%	16.7%	69.0%
Acetone	Room temp.	35.3%	13.8%	71.9%
THF	$-60^\circ C$	42.6%	14.2%	75.0%
THF	Room temp.	31.8%	14.3%	69.0%



Reactions of $(C_5H_5)Fe(\eta^5-1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadienyl})$ with triflic acid. In the dry box, $(C_5H_5)Fe(\eta^5-1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadiene})$ complex **21** (80 mg, 0.28 mmol) was dissolved in dichloromethane (2 mL) and placed in an NMR tube. The tube was covered with a rubber septum, wrapped with parafilm, and removed from the box. The solution was cooled to $-60^\circ C$, and triflic acid (18 μL , 0.28 mmol) was added via microsyringe. The solution was left standing at $-60^\circ C$ for 10 minutes. Water (19 μL , 1.05 mmol) was added via microsyringe, the tube was then shaken and placed back in the cooling bath. The reaction was allowed to warm slowly to room temperature overnight. Dichloromethane was removed under reduced pressure to afford a small amount of yellowish powder. The powder was washed with cold pentane and cold ether. The solid was then dissolved in acetone and passed through a plug of celite.

Acetone was removed at reduced pressure to yield 43 mg of two products,

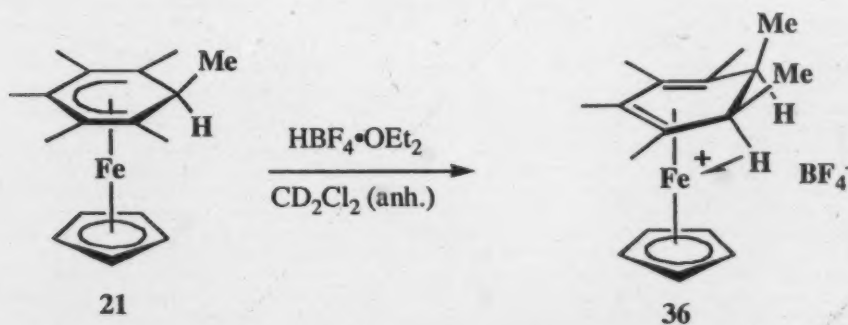
$\text{CpFe}(\text{pentamethylbenzene})^+\text{BF}_4^-$ (26.5%) and $\text{CpFe}(\text{hexamethylbenzene})^+\text{BF}_4^-$ (9.8%).

The product ratio and identities were determined by spectroscopic comparison with known literature compounds.

A second reaction was done under same conditions, varying only the temperature, as detailed in Table 2.

Table 2: Reactions of $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl})$ with Triflic acid.

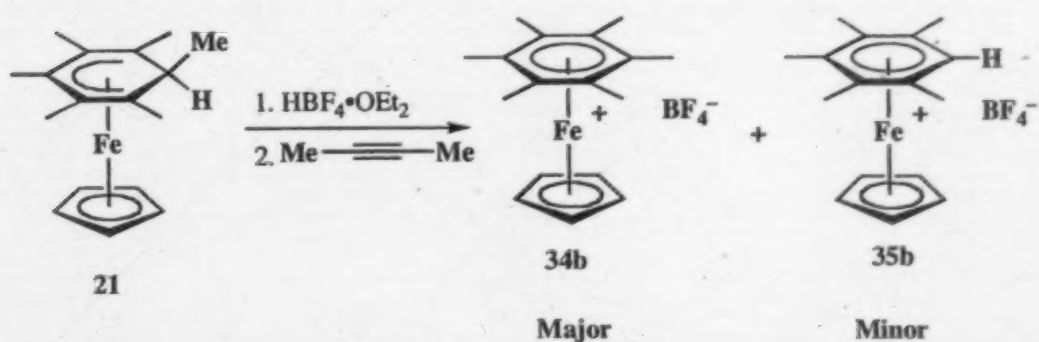
Solvent	Temperature	Yield of methyl Loss	Yield of Hydrogen Loss	Ratio of CC activation
CD_2Cl_2	-60°C	26.5%	9.8%	73.0%
CD_2Cl_2	Room temp.	27.9%	10.3%	71.5%



Reactions of $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl})$ with HBF_4 at low temperatures. Variable temperature NMR experiments

In the dry box, $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-1,2,3,4,5,6(exo)-hexamethylcyclohexadienyl})$ complex **21** (34.7 mg, 0.122 mmol) was dissolved in anhydrous deuterated dichloromethane (2 mL) and transferred to an NMR tube. The tube was capped with a small rubber septum, wrapped with parafilm, and then removed from the dry box. The solution was cooled to -78°C and $\text{HBF}_4 \cdot \text{OEt}_2$ (16.5 μL , 0.12 mmol) was added via microsyringe. After shaking,

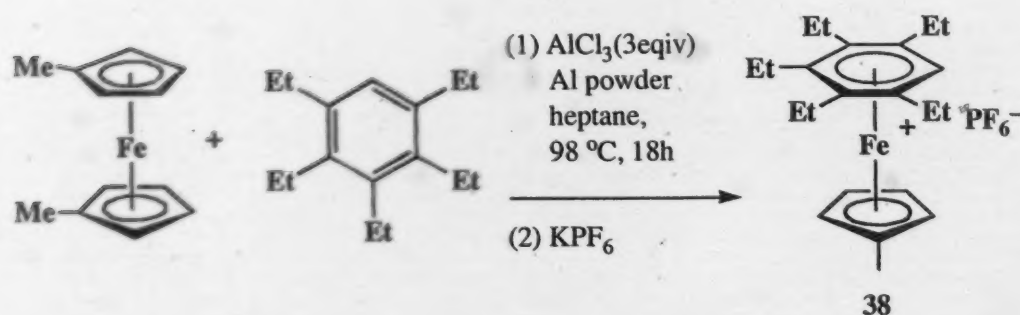
the reaction mixture was frozen in liquid nitrogen. The probe of the NMR spectrometer was pre-cooled to $-100\text{ }^{\circ}\text{C}$. The sample was then inserted. Spectroscopic data were then taken at $-80\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ in $20\text{ }^{\circ}\text{C}$ increments. ^1H NMR (400 MHz, CD_2Cl_2 , $-20\text{ }^{\circ}\text{C}$) δ 4.6 (s, 5H, 1H), 3.9 (s, 3H, CH_3), 2.1 (s, 6H, CH_3) 1.8 (s, 1H), 2.5 (s, 6H, CH_3), 0.1 (s, 3H, CH_3) -10.7 (s, 1H); ^{13}C { ^1H } NMR (100 Hz, CD_2Cl_2 , $-80\text{ }^{\circ}\text{C}$), δ 109.1 93.7, 79.9, 49.1, 42.7, 17.4, 16.8, 16.4, 14.8. The remaining spectral data remained consistent throughout all temperatures with only slight changes as discussed in results and discussion.



Reactions of $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-}1,2,3,4,5,6(\text{exo})\text{-hexamethylcyclohexadienyl})$ with HBF_4 and 2-butyne.

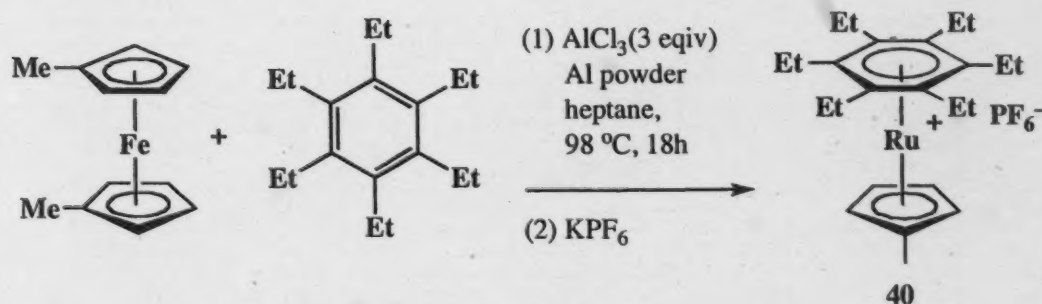
In the dry box $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-}1,2,3,4,5,6(\text{exo})\text{-hexamethylcyclohexadienyl})$ (14.2 mg, 0.0496 mmol) complex **21** was dissolved in dried degassed dichloromethane (2 mL) and transferred to an NMR tube. The tube was covered with a rubber septum, wrapped with parafilm and removed from the dry box. The solution was then cooled to $-78\text{ }^{\circ}\text{C}$ and $\text{HBF}_4\cdot\text{OEt}_2$ (6.8 μL , 0.049 mmol) was added via microsyringe. The solution was rapidly inverted, then placed back in the cooling bath for 10 minutes. Using a gastight microsyringe, 2-butyne (12.6 mg, 0.23 mmol) that had been previously condensed at $-10\text{ }^{\circ}\text{C}$ was added to the NMR tube. The NMR tube was then allowed to warm up to room temperature and stand overnight. In the drybox excess alkyne and solvent were

removed by reduced pressure. The resultant yellow solid was washed with pentane. The remaining solid was dissolved in dichloromethane and passed through a plug of celite. Upon evaporation of the dichloromethane, a mixture of the two compounds, $\text{CpFe}(\text{pentamethylbenzene})^+ \text{BF}_4^-$ and $\text{CpFe}(\text{hexamethylbenzene})^+ \text{BF}_4^-$ was found in a 32:68 ratio. The product ratio and identities were determined by NMR spectroscopic comparison to literature spectroscopic data for these compounds.¹⁸



$[(\text{MeCp})\text{Fe}(\text{pentaethylbenzene})]^+ \text{PF}_6^-$ (38). In a 500mL Schlenk flask, pentaethylbenzene (1.35 g, 6.19 mmol), dimethylferrocene (1.07 g, 5.00 mmol), and anhydrous aluminum chloride (2.2 g, 15.1 mmol), were all mixed in heptane (100 mL) resulting in an orange suspension. While stirring, aluminum powder (0.15 g, 5.56 mmol) and water (90 μL , 5.0 mmol) were also added. The mixture was then heated and maintained at reflux for 18 h, during which time a colour change from orange to green was observed. After cooling to room temperature, water (50 mL) was added very slowly with vigorous shaking, and the resultant two layers were then separated. The aqueous layer was washed with petroleum ether to remove any remaining dimethylferrocene. The aluminum salts were then precipitated from the aqueous solution by the addition of concentrated ammonium hydroxide. This created an extremely thick yellow paste. The

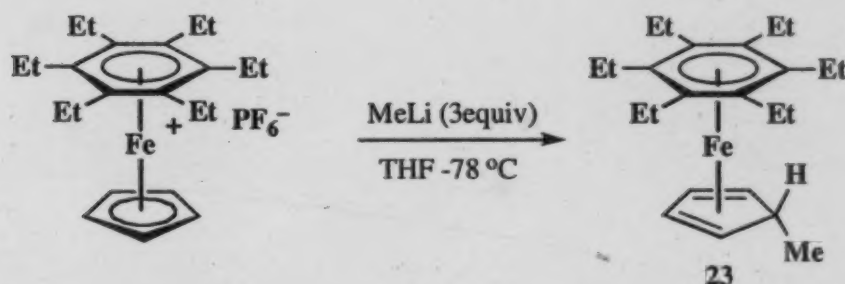
paste was filtered through celite, removing the aluminum hydroxide, and leaving a yellow solution. The yellow paste was washed with water to extract any remaining product. Upon the addition of potassium hexafluorophosphate, a yellow powder precipitated. This powder was crystallized from hot ethanol to furnish yellow needle-like crystals (0.77 g, 31%). Spectroscopic data for complex **38**: ^1H NMR (400 MHz, acetone- d_6) δ 6.18 (s, 1H), 4.77 (m, 2H), 4.69 (m, 2H), 3.07-2.81 (complex overlapping multiplets, 10H), 1.91 (s, 3H), 1.35 (t, $J = 7.6$ Hz, 3H) 1.34 (t, $J = 7.5$ Hz, 6H), 1.29 (t, $J = 7.5$ Hz, 3H); ^{13}C { ^1H } NMR (125 MHz, acetone- d_6) δ 106.1, 105.6, 104.6, 94.9, 87.5, 78.0, 77.8, 25.7, 23.4, 23.0, 16.1, 15.7, 15.6, 12.22. Anal. Calcd for $\text{C}_{22}\text{F}_6\text{FeH}_{33}\text{P}$: C, 53.03; H, 6.67. Found: C, 53.03; H, 6.59.



[(MeCp)Fe(hexaethylbenzene)] $^+\text{PF}_6^-$ (40**).** To a 500 mL Schlenk flask

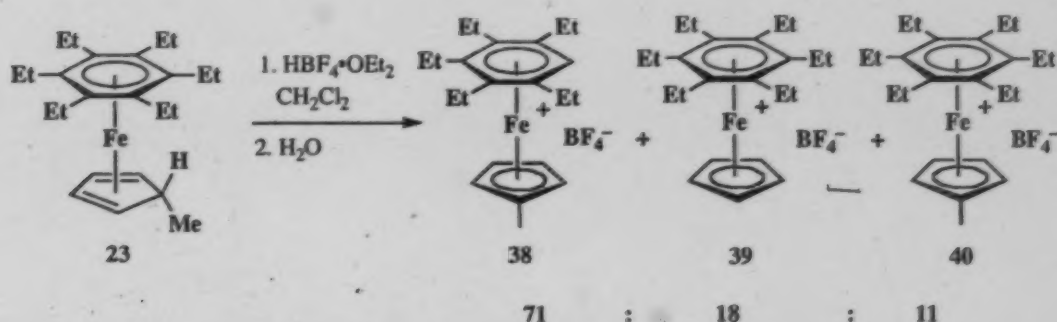
hexaethylbenzene (1.63 g, 6.62 mmol), dimethylferrocene (1.18 g, 5.51 mmol), and anhydrous aluminum chloride (2.5 g, 17.2 mmol), were all mixed in heptane (100 mL) giving an orange suspension. While stirring aluminum (0.15 g, 6.3 mmol) and water (0.1 mL, 5.5 mmol) were also added. The mixture was then heated and maintained at reflux for 18 h. After cooling to room temperature water, (50 mL) was added very slowly with vigorous shaking and the resultant two layers were then separated. The aqueous layer

was washed with petroleum ether to remove any remaining dimethylferrocene. The aluminum salts were then precipitated from the aqueous solution by the addition of concentrated ammonium hydroxide giving an extremely thick yellow paste. The paste was filtered through celite and washed with water, leaving a yellow solution. Upon addition of potassium hexafluorophosphate, a yellow powder precipitated. This powder was crystallized from hot ethanol to furnish yellow needle like crystals (1.1 g, 38%). Spectroscopic data for complex **40**: ^1H NMR (500 MHz, acetone- d_6) δ 4.74 (t, $J = 8.1$ Hz, 2H), 4.64 (t, $J = 8.3$ Hz, 2H), 3.07 (q, $J = 7.5$ Hz, 12H), 1.89 (s, 3H), 1.39 (t, $J = 7.5$ Hz, 18H); ^{13}C { ^1H } NMR (125Hz, acetone- d_6) δ 105.2, 94.6, 78.2, 78.1, 23.8, 16.3, 12.0, 18H); ^{13}C { ^1H } NMR (125Hz, acetone- d_6) δ 105.2, 94.6, 78.2, 78.1, 23.8, 16.3, 12.0, 18H); Anal. Calcd for $\text{C}_{24}\text{F}_6\text{FeH}_{37}\text{P}$: C, 54.76; H, 7.09. Found: C, 54.67; H, 7.19.



(η^6 -Hexaethylbenzene) $\text{Fe}(\eta^4$ -5(exo)-methylcyclopentadienyl) (**23**).¹⁹ This procedure is a modification of reaction conditions initially reported by Astruc. The full procedure along with spectroscopic data is located only in an unavailable Ph. D. dissertation. In a Schlenk flask under nitrogen, $[\text{CpFe}(\text{hexaethylbenzene})]^+\text{PF}_6^-$ (0.237 g, 4.6 mmol)²⁷ was dissolved in anhydrous THF (50 mL). The solution was cooled to -60°C and MeLi (13.8 mmol, 1.4 M) was added dropwise via syringe. The stirred solution was then allowed to warm up to room temperature overnight. Solvent was removed under reduced pressure to furnish a dark red brown residue. The evacuated flask was then brought into

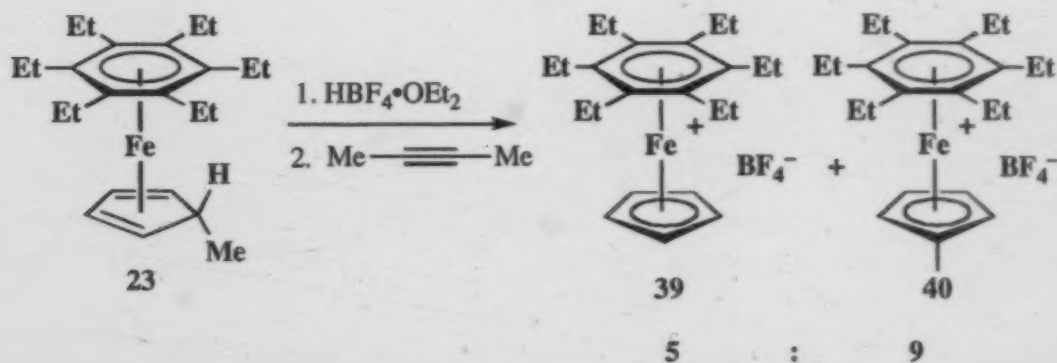
the drybox for workup. The residue was triturated three times with pentane (3×20 mL). The combined pentane fractions were then passed through small columns of celite and alumina (activity III neutral). Reduced pressure was used to evaporate the solvent to yield (hexaethylbenzene)Fe(η^4 -5(exo)-methylcyclopentadienyl) as an orange oil (0.072 mg, 40.7 %). From the ^1H NMR spectrum an impurity believed to be the methyl-substituted adduct on the hexaethylbenzene ring. Repeated attempts to isolate (hexaethylbenzene)Fe(η^4 -5(exo)-methylcyclopentadienyl) to analytical impurity by recrystallization were unsuccessful. Spectroscopic data for complex 23: ^1H NMR (300 MHz, C_6D_6) δ 4.42 (m, 2H), 2.43 (m, 1H), 2.37 (q, $J = 10.8$ Hz, 12H), 1.60 (m, 2H), 1.19 (t, $J = 10.5$ Hz, 18H), 0.45 (d, $J = 9$ Hz, 3H).



Reaction of (hexaethylbenzene)Fe(η^4 -5(exo)-methylcyclopentadienyl) with HBF_4 and H_2O .

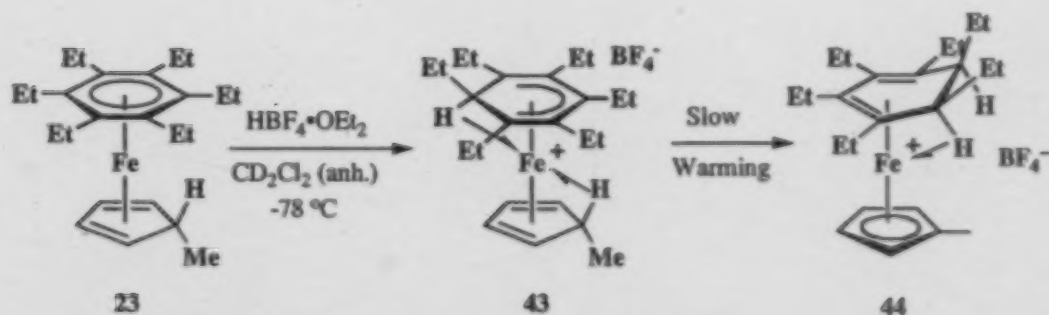
In a small vial in the dry box, (hexaethylbenzene)Fe(η^4 -5(exo)-methylcyclopentadienyl) complex 23 (21.4 mg, 0.0742 mmol) was dissolved 1 mL of CH_2Cl_2 . The orange solution was transferred to an NMR tube, which was capped with a small rubber septum, wrapped with parafilm, and removed from the drybox. The solution was then cooled to -25°C , at which point HBF_4 etherate (10 μL , 0.73 mmol) was added via microsyringe. The solution

immediately turned red. After 5 min, water (3.4 μ L, 7.5 mmol) was added via microsyringe. The solution was shaken, placed back in the -25°C bath, and then allowed to warm slowly overnight to room temperature. Solvent was removed at reduced pressure, furnishing a yellow powder. The yellow powder was washed with small amounts of cold ether, dissolved in acetone, and passed through a small celite plug. After removing the acetone at reduced pressure, a mixture of three compounds $[\text{MeCpFe}(\text{pentamethylbenzene})]^+\text{BF}_4^-$, $[\text{CpFe}(\text{hexaethylbenzene})]^+\text{PF}_6^-$, and $[\text{MeCpFe}(\text{hexaethylbenzene})]^+\text{BF}_4^-$ was obtained in a ratio of 71 : 18 : 11 in an overall yield of 38%. The products were identified by ^1H NMR spectroscopy, spiking the sample with independently-synthesized authentic samples of each product; the integration of each suspected product increased upon addition of each authentic sample.



Reaction of $(\text{hexaethylbenzene})\text{Fe}(\eta^5\text{-5(exo)-methylcyclopentadienyl})$ with HBF_4 and 2-butyne. In a small vial in the dry box, $(\text{hexaethylbenzene})\text{Fe}(\eta^5\text{-5(exo)-methylcyclopentadienyl})$ 23 (10.3 mg, 0.0272 mmol) was dissolved in dichloromethane (1 mL). The solution was transferred to an NMR tube, which was capped with a small rubber septum, wrapped with parafilm. The solution was then cooled to -25°C and

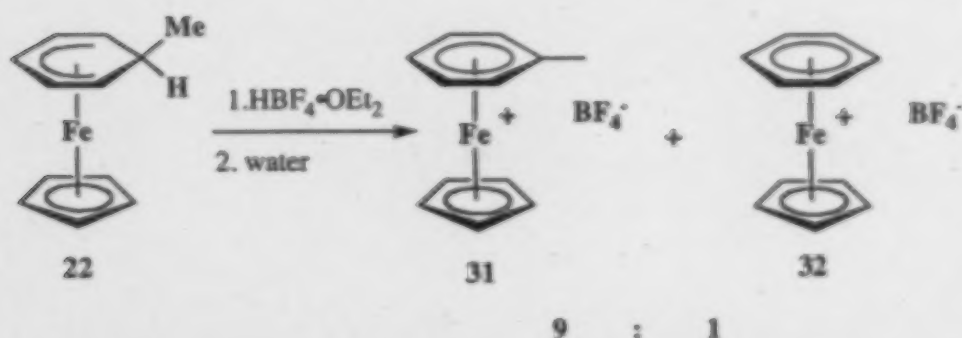
$\text{HBF}_4 \cdot \text{OEt}_2$ (10 μL , 0.73 mmol) was added via microsyringe. Using a gastight microsyringe, 2-butyne (14.8 mg, 0.27 mmol) that had been previously condensed at -10°C was added to the NMR tube. The reaction mixture was then allowed to warm to room temperature and stand overnight. In the drybox, excess alkyne and solvent were removed at reduced pressure. The resultant yellow solid was washed with pentane, dissolved in dichloromethane and passed through a small plug of celite. After the dichloromethane was removed at reduced pressure, a mixture of $[\text{CpFe}(\text{hexaethylbenzene})]^+\text{BF}_4^-$ and $[\text{MeCpFe}(\text{hexaethylbenzene})]^+\text{BF}_4^-$ was obtained in a ratio of 1 : 1.4. The products and ratio were determined by ^1H NMR spectroscopy, spiking the sample with independently-synthesized samples of each product and observing increases in the respective product signals.



Reactions of (hexaethylbenzene) $\text{Fe}(\eta^4\text{-5(exo)-methylcyclopentadienyl})$ with HBF_4 at low temperatures. Variable temperature NMR experiments.

In a small vial in the dry box, (hexaethylbenzene) $\text{Fe}(\eta^4\text{-5(exo)-methylcyclopentadienyl})$ 23 (32.3 mg, 0.0851 mmol) was dissolved in anhydrous deuterated dichloromethane (2 mL) and transferred to an NMR tube. The tube was capped with a small rubber septum, wrapped with parafilm, and then removed from the dry box. The solution was cooled to

-78 °C and $\text{HBF}_4 \cdot \text{OEt}_2$ (16.5 μL , 0.12 mmol) was added via microsyringe. After shaking, the reaction mixture was frozen in liquid nitrogen. The probe of the NMR spectrometer was cooled to -80 °C and sample was then inserted. Spectroscopic data were taken at -80 °C to room temperature in 20 °C increments, as described in the results and discussion (p. 28). Full spectra are located in appendix A.



Reaction of $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-6(exo)-methylcyclohexadienyl})$ with HBF_4 and water.

In a small vial in the dry box, $(\text{C}_5\text{H}_5)\text{Fe}(\eta^5\text{-6(exo)-methylcyclohexadienyl})$ **22**¹⁸ (52 mg, 0.24 mmol) was dissolved in dichloromethane (2 mL). The solution was shaken, transferred to a NMR tube, capped with a rubber septum, wrapped with parafilm, and removed from the dry box. The solution was then cooled to -60 °C and $\text{HBF}_4 \cdot \text{OEt}_2$ (39 μL , 0.284 mmol) was added via microsyringe. An immediate change was observed, as the solution turned much darker. After 5 min, water (11.5 μL , 1.25 mmol) was added via microsyringe. The solution was shaken, returned to the -60 °C bath, allowed to warm to room temperature, and let stand overnight. Solvent was removed under reduced pressure, leaving a yellow powder, which was washed with small amounts of pentane and cold ether. The resulting was then dissolved in acetone and passed through a small plug of celite. Upon evaporation of acetone a mixture of the two compounds $[\text{CpFe}(\eta^5\text{-6(exo)-methylcyclohexadienyl})\text{BF}_4^-]$ (31) and $[\text{CpFe}(\eta^5\text{-6(exo)-methylcyclohexadienyl})\text{BF}_4^-]$ (32) was obtained.

toluene)]⁺PF₆⁻ (10.4%) and [CpFe(η⁶-hexamethylbenzene)] PF₆⁻ (1.2%) was obtained. The product ratio was determined by spectroscopic comparison with known literature compounds.

1.4 References:

1. Milstein, D.; Rybtchinski, B. *Angew. Chem. Int. Ed.* **1999**, *38*, 870.
2. Cassar L; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1970**, 1082.
3. Kang, J. W.; Maitlis, P. M. *J Am. Chem. Soc.* **1968**, *90*, 3259.
4. Rond, D.; Chaudret, B.; He, X.-D.; Labroue, D. *J Am. Chem. Soc.* **1991**, *113*, 5671.
5. Urbanos, F.; Halcrow, M. A.; Fernandez-Baeza, J.; Dahan, F.; Labroue, D.; Chaudret, B. *J. Am. Chem. Soc.* **1993**, *115*, 3848.
6. Suggs, J. W.; Jun C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679.
7. Jun C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880.
8. Murakami, M.; Itahashi, T.; Ito, Yoshihiko, *J. Am. Chem. Soc.* **2002**, *124*, 13976.
9. Eilbracht, P. *Chem. Ber.* **1976**, *109*, 1429.
10. Rodon, D.; Chaudret, B.; He, X.-D.; Labroune, D. *J. Am. Chem. Soc.* **1991**, *113*, 5671.
11. Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *Organometallics* **1993**, *12*, 955.
12. (a) Older, C. M.; Stryker J. M. *J Am. Chem. Soc.* **2000**, *122*, 2784. (b) Older, C. M. Ph. D. Dissertation, University of Alberta, 2000.
13. Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 8275. (b) Schwiebert, K. E.; Stryker, J. M. *Organometallics* **1993**, *12*, 600. (c) Schwiebert, K. W. Ph. D. Dissertation, Indiana University, 1993.
14. Etkin, N.; Dzwiniel, T. L.; Schweibert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 9702.

15. Etkin, N.; Stryker, J. M. unpublished results.
16. Dzwiniel, T. L. Ph. D. Dissertation, University of Alberta, 1999.
17. Etkin, N.; Dzwiniel, T. L.; Stryker, J. M. *J. Am. Chem. Soc.* 1999, 121, 10640.
18. Khand, P. L.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* 1969, 116, 2024.
19. Astruc, D. *Tetrahedron*. 1983, 39, 4027.
20. Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Letters* 1963, 1725.
21. Khand, P. L.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* 1968, 115, 2257.
22. Schumann, H. J. *Organomet. Chem.* 1986, 304, 341.
23. Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V., Shubina, E. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. *J. Organomet. Chem.* 1985, 281, 349.
24. Braga, D.; Williams, J. M.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L. *J. Am. Chem. Soc.* 1980, 102, 981.
25. Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* 1987, 441.
26. Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* 1997, 119, 9393.
27. Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* 1981, 103, 758.
28. Gao, J.; Feng, Y.; Kang, J. *Synth. Commun.* 1997, 27, 3219.
29. Lázár, I. *Synth. Commun.* 1995, 25, 3181.
30. Gerald, C. F.; Sherry, A. D.; Marques, M. P.; Alpoim, M. C.; Cortes, S. *J. Chem. Soc., Perkin Trans. 2* 1991, 137.

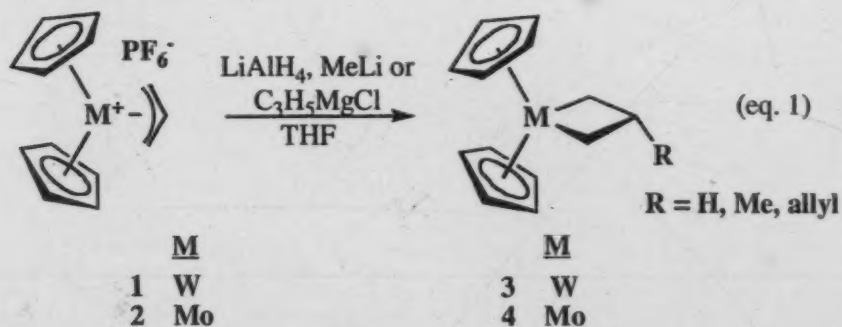
**Chapter 2 Synthesis of Bicyclic Titanacyclobutane Complexes
by Intramolecular Radical Alkylation**

2.1 Introduction: Central Carbon Attack on Allyl ligands

I. Nucleophilic Addition to Cationic Metal Allyl Complexes.

In traditional organic chemistry there are no examples of reactions at the central carbon of an allyl fragment. This can be explained by examination of the frontier molecular orbitals of the allyl species. In the case of nucleophilic attack on an allyl cation, the coefficient on the C2 of the LUMO is near zero, while the HOMO of allyl anion also has a near zero coefficient on C2. The C2 coefficients are near zero for allyls generally as a class but are zero for allyl itself. Therefore, the only way to obtain reactivity at the central carbon of an allyl compound is to drastically change the frontier molecular orbitals of the fragment. This can be done by metal complexation.

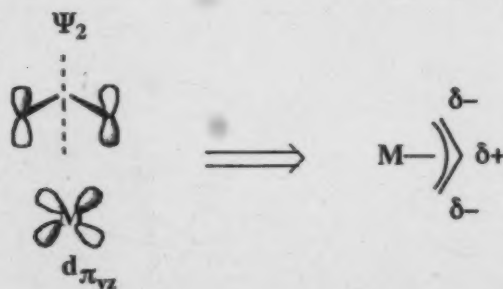
The first examples of alkylation at the central carbon of an allyl ligand involved cationic molybdocene and tungstenocene complexes discovered serendipitously by M. L. H. Green.¹ When cations **1** and **2** were treated with various nucleophiles, central carbon alkylation occurred, forming metallacyclobutanes **3** and **4** respectively (eq. 1). Terminal addition was not observed.



In order to explain this reactivity pattern, Davies, Green, and Mingos used a charge control argument.² They created a set of rules (the DGM rules), one part of which

states that on an allyl ligand, nucleophilic attack occurs at the most electron deficient carbon. In the case of complexes **1** and **2**, the central metal donates electron density to the HOMO Ψ_2 making the terminal carbons partly negative compared to the central carbon (figure 2.1).

Figure 2.1 Charge control argument for regioselectivity of nucleophilic addition.



Another system that undergoes central carbon alkylation by nucleophilic attack is the group 4 metallocene complexes, $[\text{Cp}^*_2\text{M}(\eta^3\text{-allyl})]^+$ ($\text{M}=\text{Ti}, \text{Zr}$). This chemistry was first predicted for titanium by Curtis and Eisenstein using MO energy level diagrams (figure 2.2).^{3,4} In the group 4 $[\text{Cp}^*_2\text{M}(\eta^3\text{-allyl})]^+$ metal complexes, the molecular orbital formed by interaction of the $d(3a_1)$ orbital of the metal and the π^* of the allyl is the LUMO of the complex, allowing for nucleophilic attack at the allyl C2 position.

In order to prove this prediction, the Stryker group prepared and treated cationic zirconocene π -allyl complex **5** with various nucleophiles in an effort to obtain central allyl carbon nucleophilic attack.⁵ They were met with some success, however, this chemistry only worked for bulky nucleophiles (scheme 1). When a small nucleophile was used, competitive attack occurred at the metal center to furnish an alkyl allyl zirconocene. In the case of the intermediate sized benzyl potassium, both allyl central carbon and metal alkylation occurred.

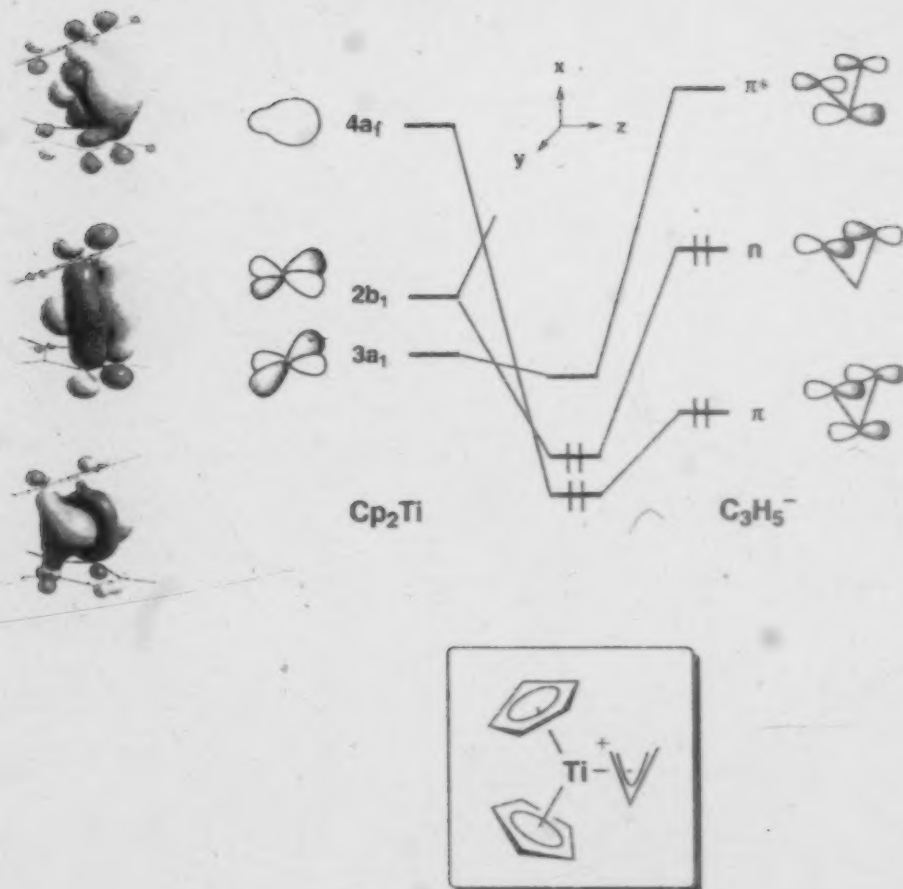
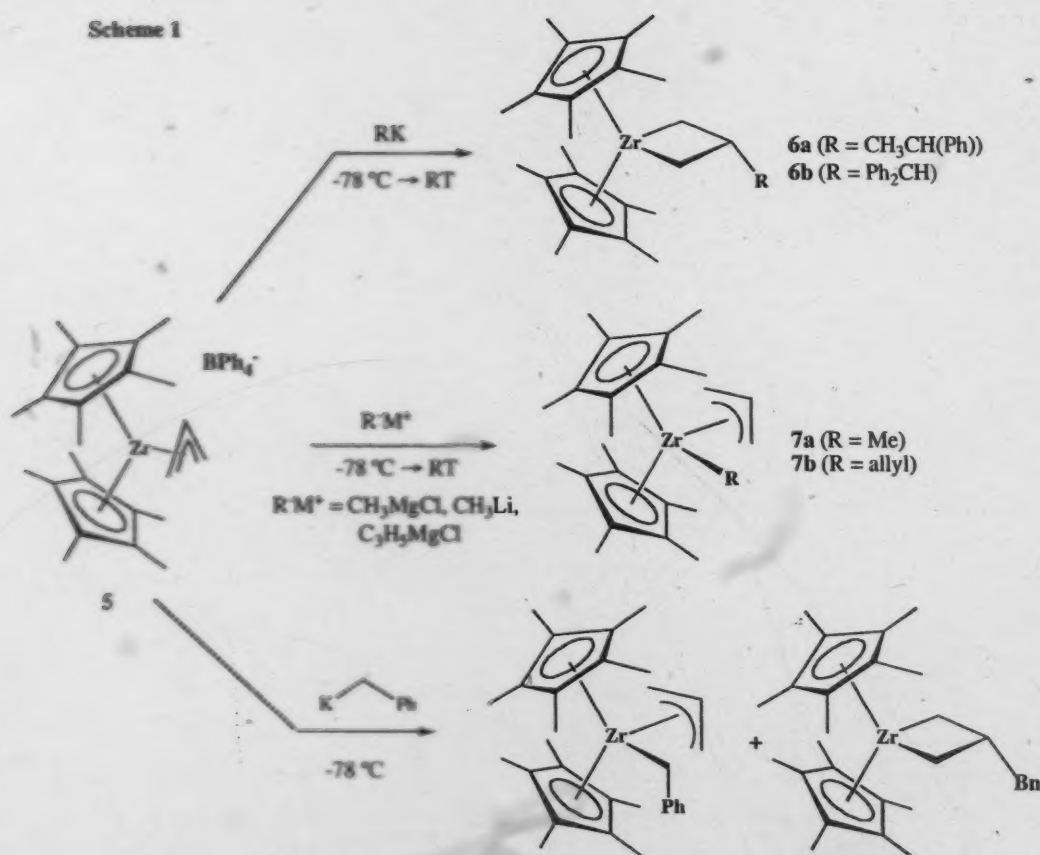


Figure 2.2 EHMO energy level diagram for d^0 group IV metallocene π -allyl complexes.

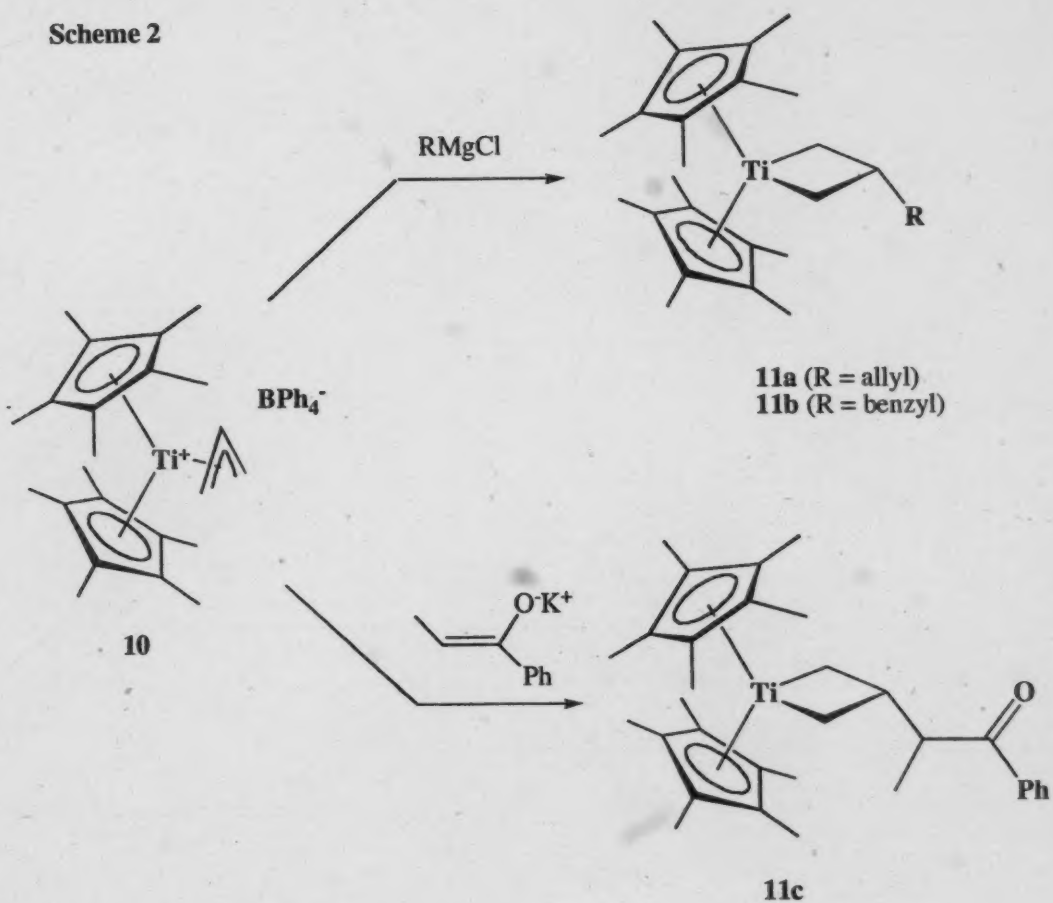
Scheme 1



When the titanium analogue of **5** was subjected to nucleophilic attack, an interesting but expected result occurred (Scheme 2).^{5,6,7} Titanium, with its smaller ionic radius, left less room for nucleophilic attack at the metal center; therefore, smaller nucleophiles also attacked the central allyl position.

Although nucleophilic attack to give titanacyclobutanes does occur, it remains subject to many limitations; (1) switching from Zr to Ti reduces but does not eliminate attack at the metal center especially for small nucleophiles such as MeLi; (2) cationic allyl complexes are hard to make and very sensitive to oxygen and Lewis bases; (3) substituted allyl complexes were unsuccessful in furnishing titanacyclobutanes.

Scheme 2



II. Radical Additions to η^3 -Allyl Complexes.

In order to overcome the limitations in the central nucleophilic addition to cationic titanium allyl complexes, neutral d^1 titanium(III) allyl complexes and radical alkylations were considered.

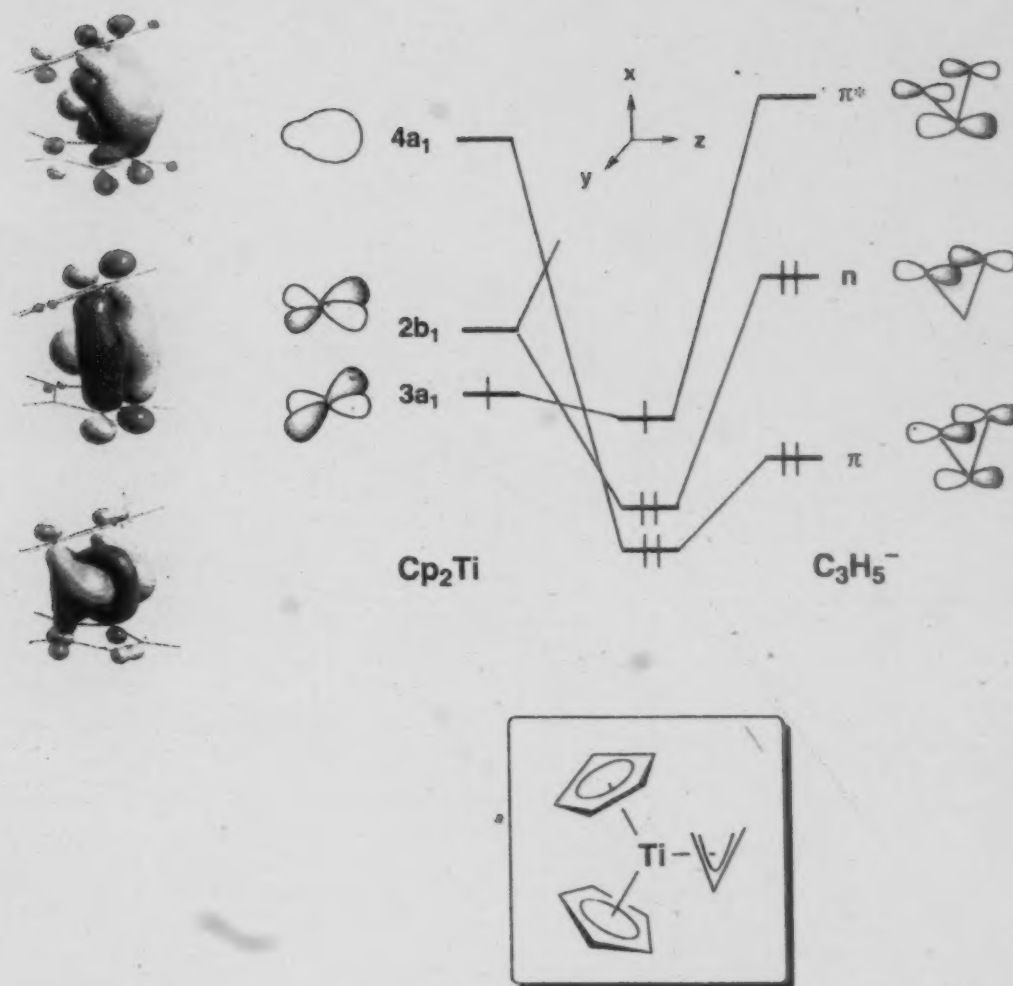
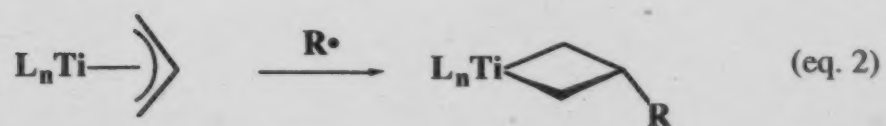


Figure 2.3 EHMO energy level diagram for d^0 group IV metallocene π -allyl complexes.

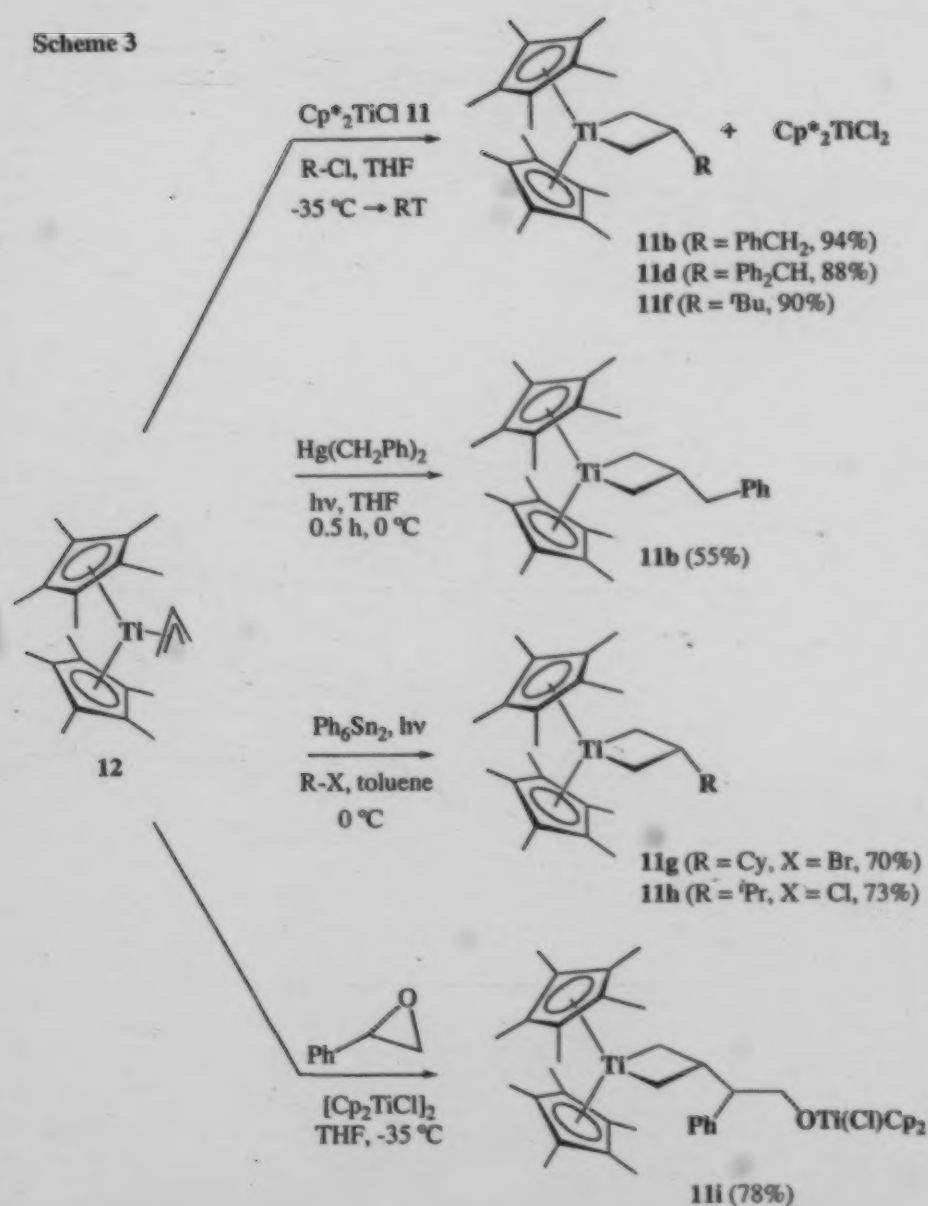


As stated above, the interaction of the $d(3a_1)$ orbital of the metal and the π^* of the allyl produces the LUMO of the cationic Ti-allyl complexes responsible for directing nucleophilic attack to the allyl C2 position. In a neutral d^1 titanium(III) allyl complex this orbital becomes the SOMO, which should allow radical reactions at the same position (Figure 2.3).^{3,4} This was first demonstrated by Casty and Stryker using $Cp^*_2Ti(\eta^3\text{-allyl})$.^{6,8} Using various radical generating processes, including (1) Cp^*_2TiCl in the presence of an alkyl halide, (2) $Hg(CH_2Ph)_2$ with photolysis,⁹ (3) Ph_6Sn_2 , with photolysis,¹⁰ (4) epoxide opening mediated by titanium (III) (Scheme 3),¹¹ and (5) SmI_2 in the presence of an alkyl halide (scheme 4),¹² titanacyclobutane complexes were obtained cleanly and in good yields.

Of the various different radical initiations, the one that proved the most broad and practical was SmI_2 in the presence of alkyl halide. Experiments done using complex 12 proved successful for a handful of different organic halides; however, it was determined that optimal reaction conditions were dependent upon the stability of the alkyl radical being formed by SmI_2 . In the case of more stabilized benzylic radicals, lower temperatures and less reactive benzyl chlorides are needed to control radical dimerization. In the case of unstablized alkyl radicals, higher temperatures and the more reactive alkyl iodide were required in order to generate titanacyclobutanes.

The use of $Cp^*_2Ti(\eta^3\text{-allyl})$ was a definite step forward because highly sensitive cationic metal complexes were no longer needed and no apparent attack occurred at the metal center. However, one major flaw in the nucleophilic addition remained shared by

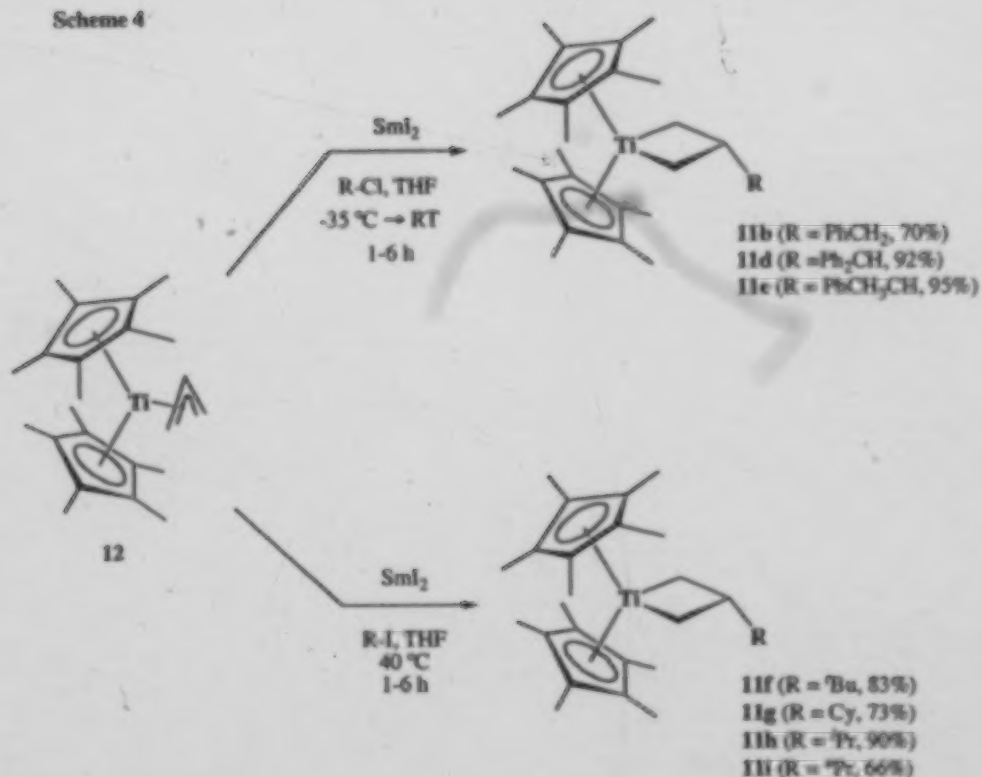
Scheme 3



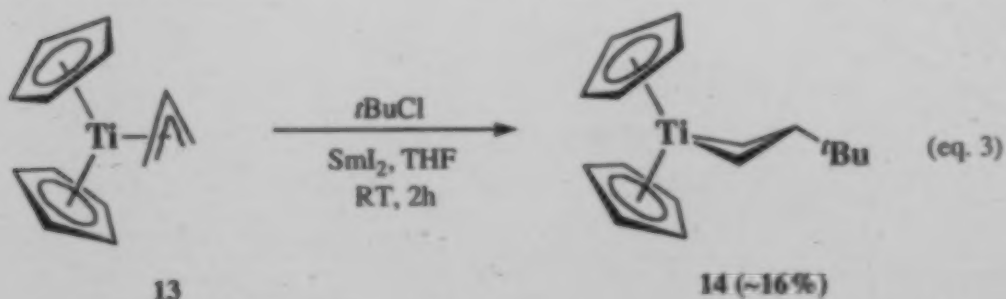
this radical addition: neither strategy tolerates substitution on the allyl ligand.^{6,7} In the hopes of solving this problem, other titanium systems were extensively investigated.

The first such system was $\text{Cp}_2\text{Ti}(\eta^3\text{-allyl})$ 13. The main advantage of complex 13 is the relative availability of Cp in comparison to Cp^* .⁶ Secondly, Cp has a much smaller

Scheme 4



steric profile than Cp^* ; therefore, it has much more room to accommodate η^3 -coordination of a substituted allyl ligand. Unfortunately, very little success was obtained using this system. In fact, there was only one case in which a titanacyclobutane was obtained. This occurred for the reaction of *tert*-butyl chloride with $\text{Cp}_2\text{Ti}(\eta^3\text{-allyl})$ in the presence of SmI_2 (eq. 3).

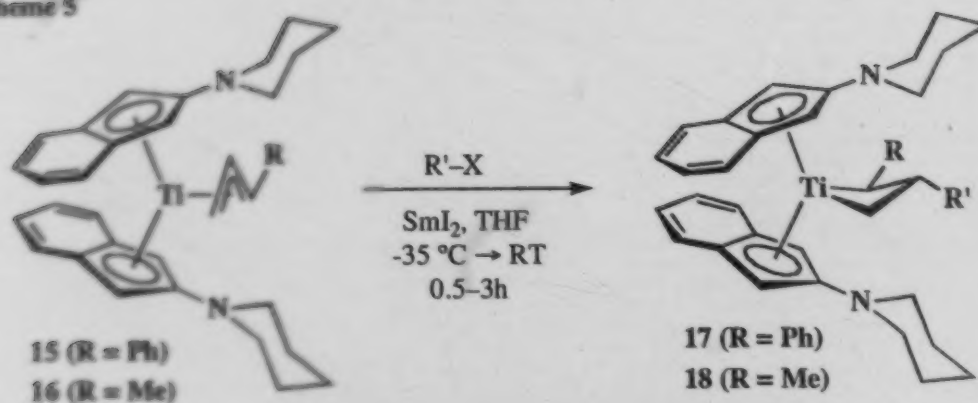


Because of this lack of reactivity, the Stryker group concluded that some minimum level of electron density appeared to be required to allow sufficient $d \rightarrow \pi^*$ backbonding to facilitate central carbon radical attack. This backbonding was important to help inhibit the allyl from undergoing a coordination change from η^3 to η^1 and to help drive the oxidation of Ti(III) to the higher oxidation state Ti(IV) products. The η^3 to η^1 isomerization in group 4 allyl metal coordination is known to be facile and has been observed for both zirconium and titanium metallocenes.¹³

Among the electron rich systems which were examined for titanacyclobutane formation was the bis(2-piperidinoindenyl)titanium(III) template.¹⁴ It was hoped that the new 2-piperidinoindenyl ligand would donate sufficient electron density to the metal center while still leaving enough room for substituted η^3 -allyl ligands to bind in an η^3 -fashion. The 2-piperidinoindenyl ligand was chosen over structurally simpler aminocyclopentadienyl ligand because $C_5H_5NR_2$ is very difficult to make. In order to test the reactivity of substituted allyls, crotyl and cinamyl complexes **15** and **16** were synthesized. Reactions of **15** and **16** with *tert*-butyl chloride, 2-iodopropane and iodocyclohexane furnished the expected titanacyclobutanes **17a-c** and **18a-c** (Scheme 5). Unfortunately, the titanacyclobutane complexes formed from crotyl complex **15** had very short lifetimes, which was attributed to β -hydride elimination from the accessible β -hydrogen atoms on the methyl group, possibly driven by the sterically large piperidino ligand.

Many other η^3 -allyl templates were assayed for the ability to facilitate titanacyclobutane formation. Titanocene systems that were evaluated included several ansa-bridged systems,^{15,7} bis(*tert*-butylcyclopentadienyl)titanium(III),³ (cyclopentadienyl)(pentamethylcyclopentadienyl)titanium(III),¹⁶

Scheme 5



Starting complex	R'X	Product	Yield
15	$tPrI$	17a	72%
15	CyI	17b	80%
15	$tBuCl$	17c	88%
16	$tPrI$	18a	69%
16	CyI	18b	70%
16	$tBuCl$	18c	36%

bis(2-methoxyindenyl)titanium(III),¹⁷ and bis(2-N,N-dimethylaminoindenyl)titanium(III) η^3 -allyl complexes.¹⁷ All provided varying degrees of success but none seemed to be the definitive answer to all the problems associated with titanacyclobutane formations. Among these, the *N,N*-dimethylaminoindenyl system functioned with the greatest generality.¹⁷

However, one very interesting discovery was made by extensive crystallographic analysis of the bis(2-*N,N*-dialkylaminoindenyl) and the bis(2-piperidinoindenyl)titanium(III) templates.^{17,18} The solid state structures clearly show that the amine nitrogens are substantially pyramidal, not planar, and the potentially donating

lone pair orbitals are rotated significantly out of the indenyl plane, making them much weaker electron donors than expected.

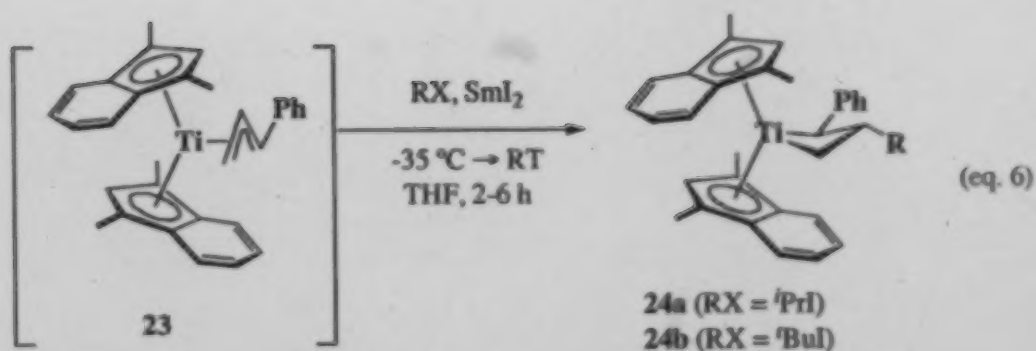
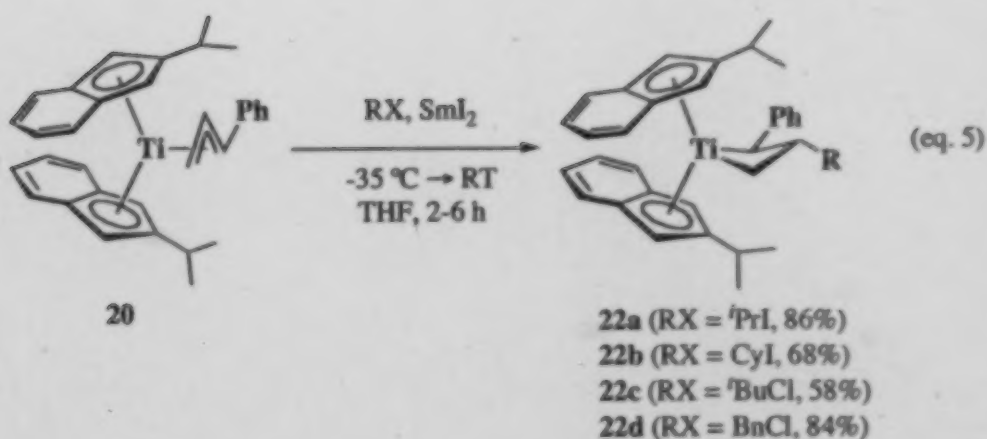
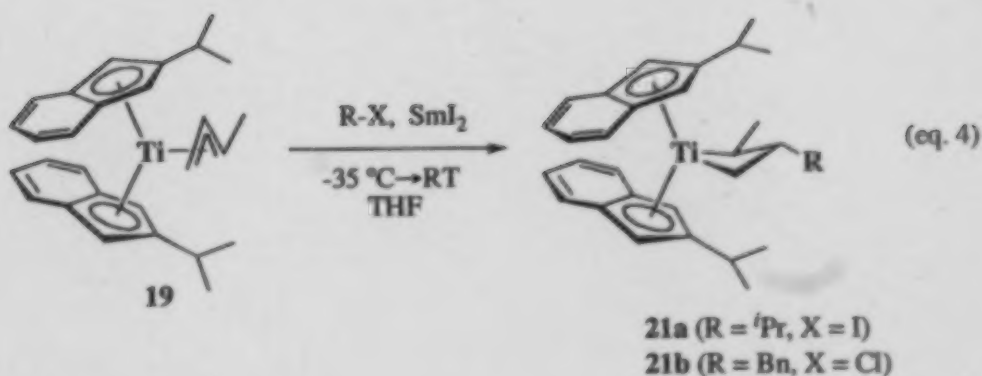
These crystallographic data led to the investigation of simple, less electron donating 2-alkyl-substituted indenyl ligands. The first ligand that was investigated was the pseudo-isosteric 2-isopropylindenyl ligand. Using this ligand, titanium complexes **19** and **20** were prepared with both η^3 -crotyl and η^3 -cinnamyl substrates. Surprisingly, both substituted allyl complexes underwent radical attack at the central position to form titanacyclobutanes (eq. 4 and 5). However, β -hydride elimination was again a problem in the crotyl-derived case.

The 1,3-dimethylindenyl ligand showed similar results. Cinnamyl complex **23**, prepared *in situ* (see below) furnished titanacyclobutanes upon addition of isopropyl iodide, *tert*-butyl iodide, or benzyl chloride in the presence of SmI_2 . The complexes formed in these reaction appear to be indefinitely stable (eq. 6).¹⁹

III. One-pot All-Samarium Mediated Synthesis of Titanacyclobutane Complexes

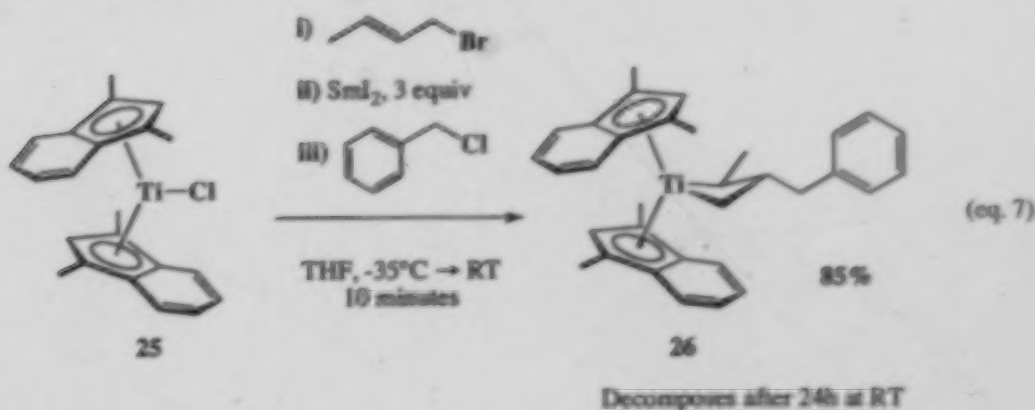
In the above radical reactions to form titanacyclobutane complexes, the allyl titanium(III) complex is formed first and isolated. The allyl is normally prepared by addition of a lithium or magnesium allyl reagent to the titanocene chloride complex. The titanium allyl complex is then treated subsequently with an organic halide in the presence of SmI_2 to furnish the titanacyclobutane.

A method of generating the allyltitanium intermediate *in situ* was first developed by Chen in the Stryker group.²⁰ This procedure involves a one-pot synthesis of the titanacyclobutane mediated only by SmI_2 . In the first step, the titanocene monochloride is



mixed with an allyl halide at $-35\text{ }^\circ\text{C}$. After one minute of stirring, three equivalents of Sml_2 are added, followed by immediate addition of the alkyl halide. One example of this process is illustrated, involving complex **25** and benzyl chloride, forming the

titanacyclobutane **26** (eq. 7).¹⁹ This titanacyclobutane complex was the most stable of the crotyl complexes formed in this series. Complex **26** was still susceptible to β -hydride elimination, however, it survived long enough to allow both ^1H and ^{13}C NMR spectroscopic characterization. If **26** is stored at -35°C , only slight degradation is detected in the ^1H NMR spectrum after 24 hours. It should also be noted that the starting titanium complex **25** may be dimeric rather than monomeric, as depicted.

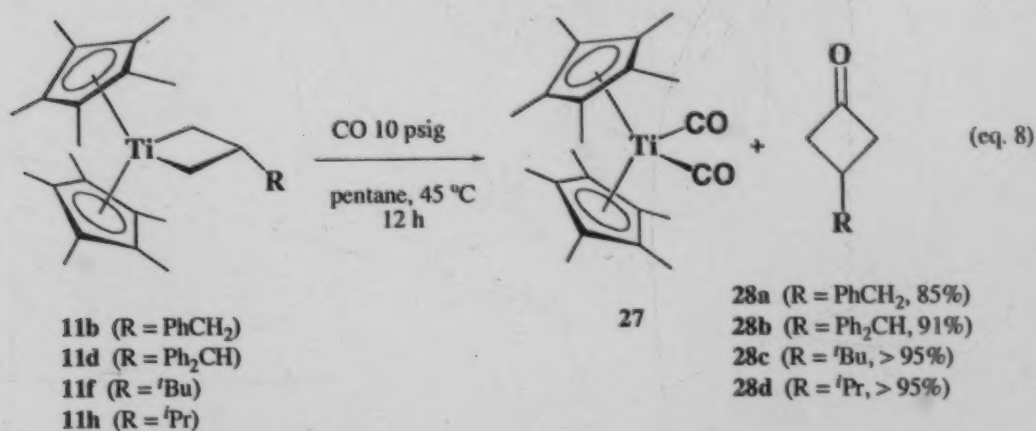


IV. Small Molecule Insertion into Titanium-carbon Bonds of Titanacyclobutanes Complexes

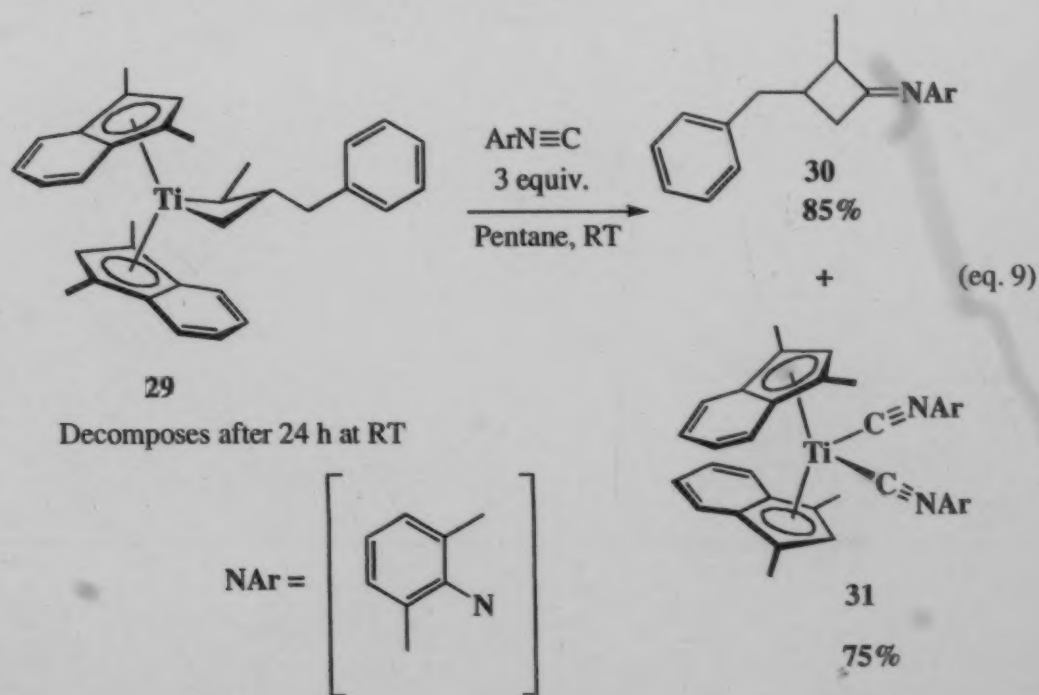
Four-membered organic ring synthesis is both an important and interesting challenge to synthetic chemists. As a result of this and the fact that many of the titanacyclobutane complexes are susceptible to decomposition by β -hydride elimination, it was important to be able to convert the titanacyclobutane directly into organic products. Two of the methods that have been developed to accomplish this transformation involve the insertion of small polar molecules into the titanium-carbon bond.

The first functionalization method proceeds by the insertion of carbon monoxide under low pressure. Under these conditions, 3-alkyltitanacyclobutane and 2,3-

disubstituted titanacyclobutane complexes furnish two products: the organometallic dicarbonyl complex, $\text{Cp}^*_2\text{Ti}(\text{CO})_2$, and the organic cyclobutanone (eq. 9).²⁰

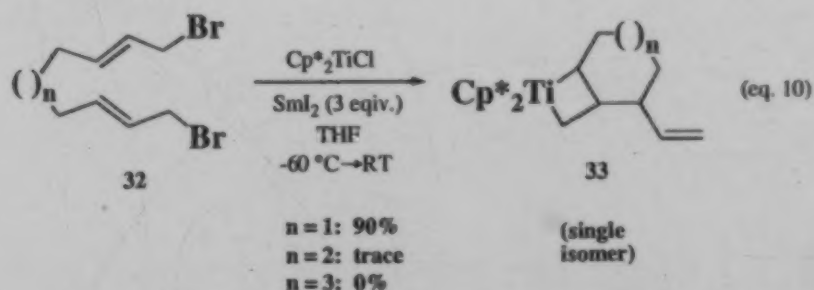


Similarly, isonitrile insertion also furnishes four membered organic rings in the form of cyclobutananimines.¹⁸ Norman has used this method to obtain the organic product 30 from the unstable 29 at room temperature.¹⁹ In this reaction, the titanium is recovered in good yield as the bis(isonitrile) complex 31 (eq. 9).



V. Intramolecular Alkylation to give Bicyclic Titanacyclobutane Complexes

Some attempts have been made to extend titanacyclobutane formation to an intramolecular process, forming a bicyclic titanacyclobutane complexes. The pentamethylcyclopentadienyl system could be used successfully to generate a bicyclic titanacyclobutane product in excellent yield (eq. 6, $n=1$). However, this reaction pattern proved to be an isolated example, as extended substrates furnished at best trace amounts of product. Thus the only successful example was garnered by treatment of the titanocene monochloride with 1,8 dibromo-1,2-octadiene **32** in the presence of SmI_2 (eq. 10). Attempts to make the larger bicyclic systems in which the B-ring contained 7 or 8 carbons were unsuccessful.



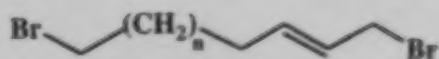
One possible reason for this lack of larger ring products could be the reversibility of the allyl radical attack on the central carbon of the allyl bound to titanium. Greidanus has recently shown that reversibility of radical addition can occur when the radical fragment is highly stabilized in nature, as in the case of allyl or benzyl.¹⁷

Project Goals

The primary goal of this investigation was to evaluate the 1,3-dimethylindenyl ligand system developed by Norman as a system for bicyclic titanacyclobutane formation. It was hoped that this system would prove to be more general than the Cp^*_2TiCl system, based on the improved compatibility of the indenyl system for alkylation of substituted allyl complexes.

In order to avoid the possibility of reversibility in the titanacyclobutane formation, the simpler bis(bromide) substrates **34** with primary terminal bromide functionality were selected.

Figure 2.4 : Substrate targets for bicyclic titanacyclobutanes



34a $n=1$

34b $n=2$

34c $n=3$

2.2 Results and Discussion

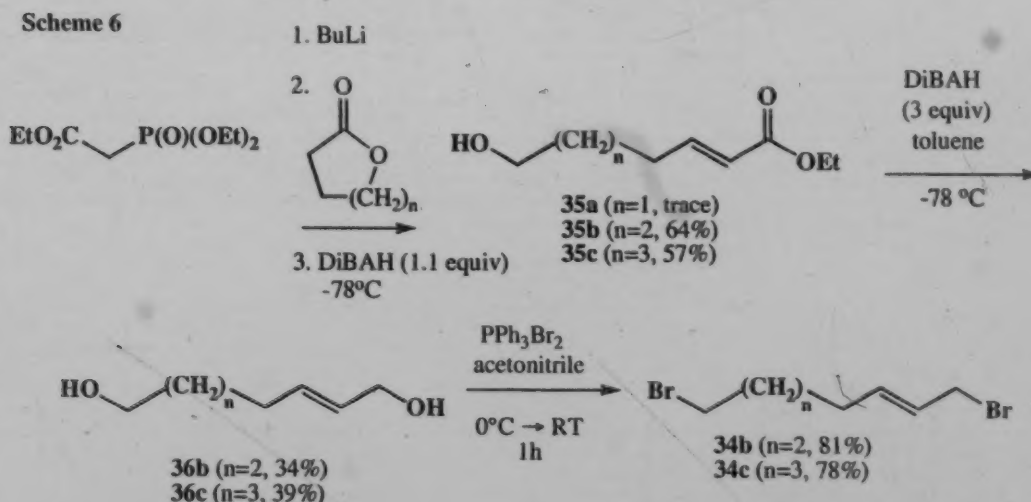
I. Substrate Synthesis

To synthesize *trans*-1,6-dibromo-2-hexene, *trans*-1,7-dibromo-2-heptene and *trans*-1,8-dibromo-2-octene **34a-c**, the procedure of Takacs, *et al.*, for was used to accomplish the two carbon homologation of an esters to α,β -unsaturated esters, a procedure also effective for lactones.²¹ In this procedure, the lactone is added to a solution of deprotonated triethylphosphonoacetate at -78°C . The reaction mixture is then slowly treated with DiBAH in order to reduce the lactone to the lactol. The open chain form of the lactol then reacts with the Wittig reagent, furnishing the α,β -unsaturated ester. Duplicating the procedure described by Takacs, we were able to obtain α,β -unsaturated esters **35b** and **35c** in comparable yields using ϵ -caprolactone and δ -valerolactone as starting materials (Scheme 6). However, use of the smaller γ -butyrolactone resulted only in a trace yield of **35a**. This may be due to the fact that the γ -butyrolactol remains entirely in its cyclic form and is thus unable to react with the Wittig reagent. Attempts to drive the conversion by heating the reaction mixture after the addition of the DiBAH proved unsuccessful.

The next transformation was the reduction of the α,β -unsaturated ester to the corresponding allylic alcohol. Takacs demonstrated that modifying the above procedure by increasing the amount of DiBAH from one equivalent to 3.2 equivalents resulted in the formation of the allylic alcohol when starting from an open chain. We tried to carry this reactivity pattern forward to the lactones, however, allylic alcohols were not

obtained. Instead, **35b** and **35c** were purified and then reduced in a separate reaction at $-78\text{ }^{\circ}\text{C}$ with DiBAH to furnish diols **36b** and **36c**. The yields for these reactions were low, but sufficient material was obtained for our investigation, and optimization of the reaction was not investigated.

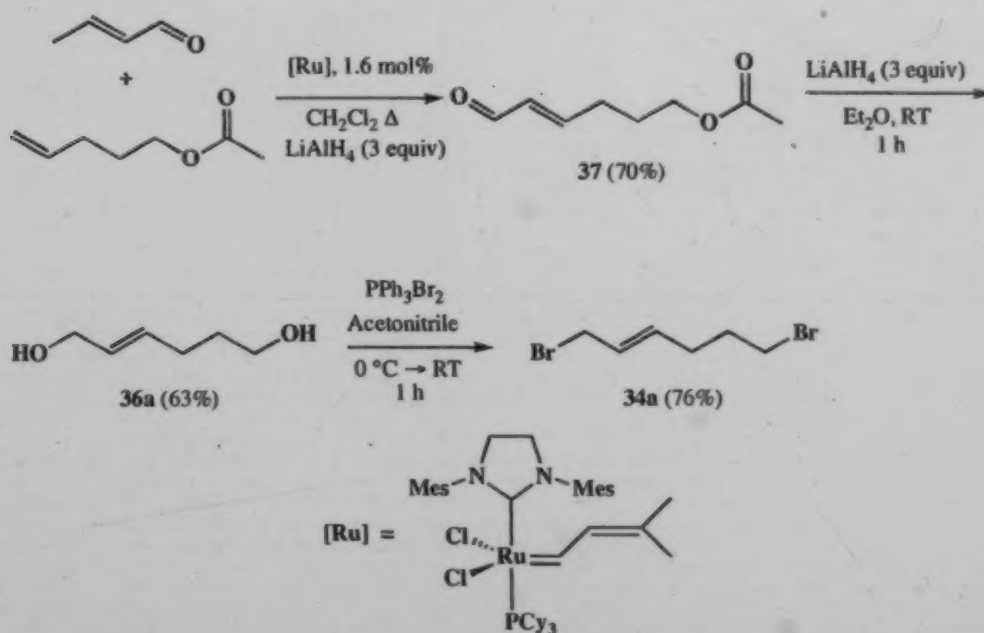
The last step, furnishing the targeted dibromo compounds **34b** and **34c**, involved a simple functional group interchange. This was accomplished by using triphenylphosphine mixed with an equal amount of bromine, to which the diol was added. The yields obtained for these reactions were good and in most trials only the terminal allyl bromide was obtained. In the few cases when some *trans*-1,6-dibromo-7-octene was evident in the ^1H NMR spectrum, separation was not attempted because both allylic bromides should furnish the same allyl titanium species. The final products **34b** and **34c** were obtained in overall yields from starting materials of approximately 17%.



In order to obtain *trans*-1,6-dibromo-2-hexene **34a**, a new synthetic strategy had to be developed, due to the failure of butyrolactone to produce any significant yield of α,β -unsaturated ester **35a**. To accomplish this we turned to olefin metathesis, using the

second generation Grubbs' catalyst.²² Heating a mixture of acrolein, 4-pentenyl acetate and two mole percent Grubbs' catalyst to reflux in dichloromethane produced only 50% conversion after 24 h. The reaction could be driven to completion by adding more acrolein and catalyst. However, switching from acrolein to crotonaldehyde resulted in higher yields of the cross metathesis product **37** and required lower catalyst loading (Scheme 7).

Scheme 7



The product **37** of the metathesis reaction was then treated with LiAlH_4 to reduce the ester and aldehyde functionality and to furnish *trans*-2-hexene-1,6-diol **36a**. The diol was then converted to *trans*-1,6-dibromo-2-hexene using PPh_3Br_2 , the same procedure used to prepare larger chain dibromide substrates. This second synthetic pathway, produced an overall yield of allylic bromide (~35%) that was twice that obtained with the lactone procedure and will likely be better for horologes as well. This method may

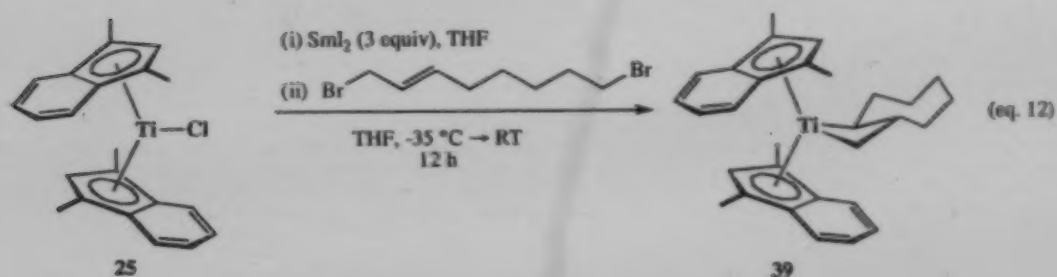
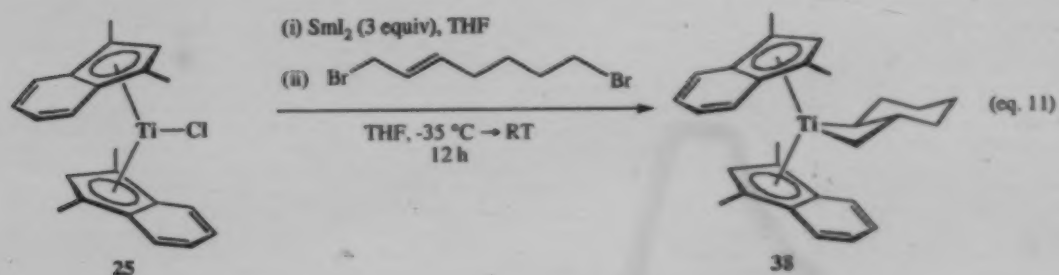
also allow access to more complex substrates needed to create other substituted bicyclic titanacyclobutanes.

II. Formation of Bicyclic Titanacyclobutane Complexes via Radical Alkylation

In our first attempts to make bicyclic titanacyclobutanes, equimolar amounts of the allylic bromide and bis(1,3-dimethylindenyl)titanium(III) chloride were mixed, followed by addition of 3 equivalents of SmI_2 . This proved unsuccessful, providing no titanacyclobutane formation. During this reaction, the colour of the mixture changed from green to brown, instead of the red colour normally observed during titanacyclobutane formation. It is thus possible that a titanium (IV) allyl intermediate initially forms, but is not stable enough to survive any length of time. We surmised that if the reaction was carried out in the presence of reductant (SmI_2), this unstable species might be trapped by reduction to immediately a more stable Ti(III) allyl complex before decomposing.

Our next attempt to produce titanacyclobutane thus involved mixing the titanium complex with the SmI_2 and then adding the allyl bromide at -35°C . The reaction mixture was maintained for one hour at -35°C with periodic mixing, then removed from the freezer and allowed to warm to room temperature for 12 h with constant stirring. Using this method, 1,1'-[bis(1,3-dimethylindenyl)]titanabicyclo[4.2.0]octane **36** and 1,1'-[bis(1,3-dimethylindenyl)]titanabicyclo[5.2.0]nonane **37** were obtained from 1,7-dibromo-2-heptene and 1,8-dibromo-2-octene, respectively, in good yield after filtration to remove the solid samarium(III) precipitate and evaporation to remove THF (eqs. 11 and 12). When this procedure was repeated using the shorter chain 1,6-dibromo-2-

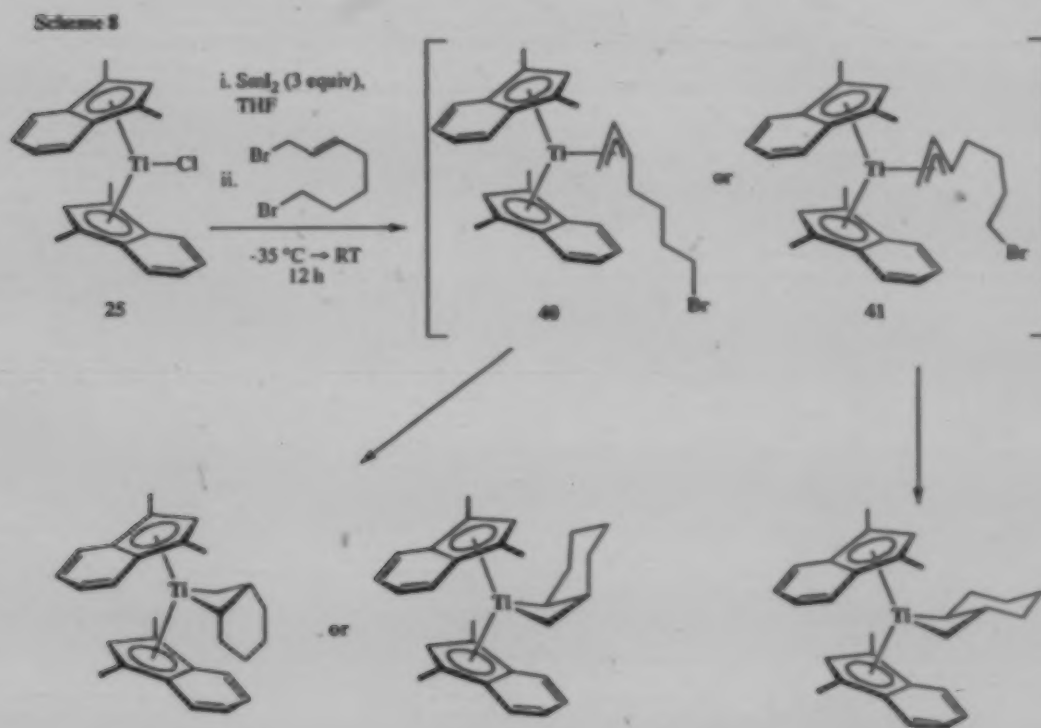
hexene **34a**, no titanacyclobutane complex was observed, even upon modification of the reaction concentrations and time.



The two titanacyclobutane complexes **38** and **39** were quite stable with respect to β -hydride elimination. Complex **38** survives indefinitely at $-35\text{ }^{\circ}\text{C}$, while seven-membered ring **39** showed only slight degradation after 36 hours at $-35\text{ }^{\circ}\text{C}$. This is not surprising, as it is expected that the more rigid bicyclic structure would inhibit the molecule from attaining the roughly co-planar geometry required for β -hydride elimination. The fact that the titanabicyclo[5.2.0]nonane is less stable than the titanabicyclo[4.2.0]octane system is consistent with this hypothesis, as the larger seven membered ring is conformationally less constrained.

From the NMR spectral data, we were not able to unambiguously identify the stereochemistry at the ring junction. Many attempts to crystallize the two compounds were made; however, no crystals suitable for X-ray diffraction could be obtained, presumably due to the highly hydrophobic nature of the materials. The stereochemistry

obtained from these reactions is dependent on the stereochemistry of the intermediate allyl complex (Scheme 8). Thus, if the allyl intermediate adopts the thermodynamically preferred *syn* orientation, the *trans*-fused product is expected, while an *anti* intermediate will provide the *cis*-fused product. We tentatively assign the stereochemistry of the products to contain the *trans* ring junction, supported by several arguments discussed below.



The *trans* stereochemistry is not energetically unreasonable because the metal-carbon bonds in the four-membered ring are much longer than normal carbon-carbon bonds and the natural C-Ti-C bond angle are much smaller than in a cyclobutane ring, resulting in strain energy similar to a purely organic [4.3.0] carbocycle. Residual strain certainly might make the *cis* counterpart more thermodynamically stable, but, we suspect, not by a significant amount.

One argument supporting the *trans* stereochemistry is that all other titanacyclobutane complexes derived from substituted allyl intermediates, which have been fully characterized, have resulted from allyl intermediates of the *syn* stereochemistry. All fully characterized 1,2-disubstituted titanacyclobutane complexes furnished have been *trans* products.

A second clue suggesting that the ring junction obtained in both complexes **38** and **39** is indeed *trans* is the failure of the reaction that would have led to the titanabicyclo[3.2.0] bicyclic system. If the geometry of the intermediate allyl were *syn*, it would be difficult for the tethered terminal radical to reach around to accomplish central carbon attack, with a tether only three carbons long. However, this attack appears reasonable from the *anti* geometry, which would result in a *cis* ring junction formation. Therefore, the fact that we did not get a titanacyclobutane product from the reaction of 1,6-dibromo-2-hexene with the dimethylindenyl titanium complex **25** suggests that it may have adopted the *syn* geometry characteristic of all titanium allyl complexes characterized to date.

The spectroscopic data for complex **38** are consistent with the product assignment and *trans* stereochemistry, and the ^{13}C or ^1H NMR spectra show no evidence of major impurities.

Figure 2.3: Structures for comparison of ^1H NMR spectral data in Table 2.11

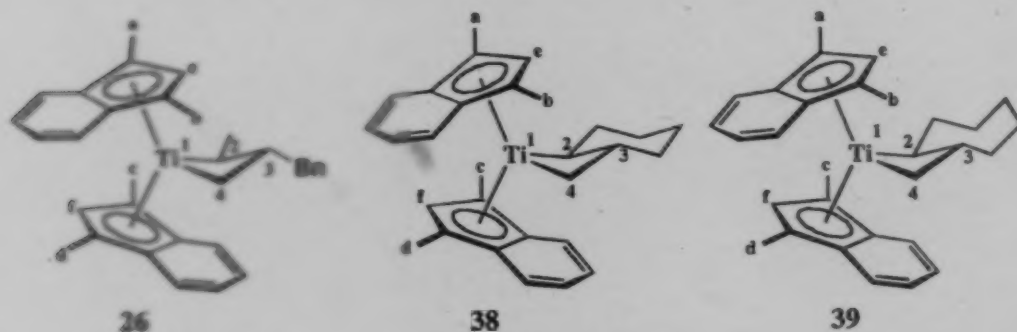


Table 2.1: ^1H NMR comparison data between complexes 26, 38, and 39

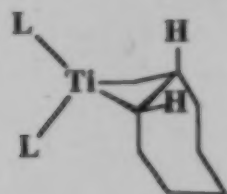
^1H NMR signal	Complex 26 δ (ppm)	Complex 38 δ (ppm)	Complex 39 δ (ppm)
2	-1.89	-1.36	-0.98
3	-0.79	-1.88	-1.76
4	2.19, 1.92	1.96, 1.44	2.44, 1.89
a, b, c, d	2.15, 1.99, 1.90, 1.82	2.31, 2.16, 2.14, 2.12	2.22, 2.14, 2.09, 1.97
e, f	5.21, 3.13	5.90, 3.81	5.15, 3.29

Comparison of the ^1H NMR spectrum of 1,1-[bis(1,3-dimethylindenyl)]titanabicyclo[4.2.0]octane **38** with the well-characterized bis(1,3-dimethylindenyl)(3-benzyl-2-methyl)titanacyclobutane **26**¹⁹ shows the strong similarities. Both compounds have upfield signals for the hydrogens on the tertiary carbon attached to titanium (C-2 carbon). The signal in the titanabicyclo [4.2.0] complex **38** appears at δ

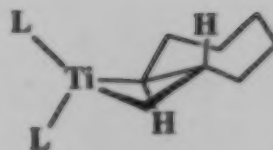
-1.36, while in monocyclic **26**, it appears at δ -1.89. The hydrogens atoms attached to the other carbon bonded to titanium (C-4) occur at δ 1.96 and δ 1.44 in titanabicyclic **38**. These are only somewhat upfield from the corresponding hydrogen atoms in **26** which occur at δ 2.19 and δ 1.92. Both compounds show four separate signals for the methyl groups attached to the indenyl ligands, appear at δ 2.31, δ 2.16, δ 2.14, and δ 2.12 in **38** and at δ 2.15, δ 1.99, δ 1.90, and δ 1.82 in **26**. The signals attributed to the two hydrogens in the 2-position of the each indenyl ligands are quite similar for each complex. In complex **38** they appear at δ 5.01 and δ 3.81, respectively, while in complex **26** they are found in reasonably similar positions at δ 5.21 and δ 3.13. Both compounds have a complex overlapping multiplet in the aromatic region, revealing little of, structural relevance.

The ^1H and ^{13}C NMR spectra of 1,1-[bis(1,3-dimethylindenyl)]titanabicyclo[5.2.0]nonane **39** show similar defining characteristics, again with little evidence for impurities. One major difference in this data was that more fine coupling was seen in the ^1H NMR spectrum for the bridgehead hydrogen atoms. The hydrogen on the tertiary carbon attached to titanium shows three coupling constants of $\sim J = 10.5$ Hz, 10.5 Hz and 5 Hz. The existence of two large and one small coupling suggests that we do in fact have the trans fused ring (Figure 2.5), as *cis*-fused ring would be expected to display two smaller and one larger coupling (Figure 2.5).

Figure 2.5: *trans* vs *cis* ring junctions geometry



cis-fused ring



trans-fused ring

Attempts to obtain elemental analyses for the both compound **38** and **39** proved unsuccessful, as they decomposed rapidly in air. The mass spectrometric data was consistent for the composition of compound **39**, however, we were not able to locate the molecular ion peak. Instead peaks were observed corresponding to the *bis*-dimethyl indenyl titanium fragment $C_{22}H_{22}Ti^+$ and the bicyclic ring loss fragment $C_8H_{14}^+$. In the mass spectrum of compound **38** we were able to find only the $C_{22}H_{22}Ti^+$ fragment ion and no molecular ion peak.

Thus, the identification and stereochemistry of both the complexes **38** and **39** remain tentative, but accumulated circumstantial evidence clearly suggests both the structure and the stereochemistry have been correctly assigned.

III. Isocyanide insertion

To separate and fully characterize the organic component of both complexes **38** and **39**, isocyanide insertion was attempted. We hoped to determine the stereochemistry at the ring fusion, assuming it would be conserved upon insertion. Secondly, it was important to demetallate the organic fragment to demonstrate synthetic potential. Both **36** and **39** were treated with three equivalents of 2,6-dimethylphenylisocyanide but no bicyclic organic product could be recovered. Increasing the amount of isocyanide also

proved unsuccessful. The products obtained from these reactions were not characterized, but comparison of the NMR spectra of starting materials and products showed complete disappearance of the starting material. We suspect the formation of paramagnetic Ti(III) products, but no further investigations have as yet been carried out.

It appears that the 1,3-dimethylindenyl ligand system developed by Norman works well for the formation bicyclic titanacyclobutanes. Though the stereochemistry at the ring junction is not yet unambiguously identified, it is clear we have produced a single isomer. It is clearly important to identify this stereochemistry and extend this methodology to more complicated substrates and new demetallation procedures.

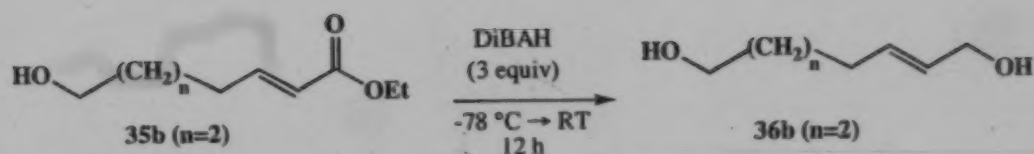
2.3 Experimental Procedures

Reagents and Methods. The methods used are the same as those outlined in the Iron chemistry experimental procedures.

The following compounds were prepared by published procedures: *trans*-7-hydroxy-hept-2-enoic acid ethyl ester,²¹ *trans*-8-hydroxy-octa-2-enoic acid ethyl ester,²¹ tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV)dichloride.²²

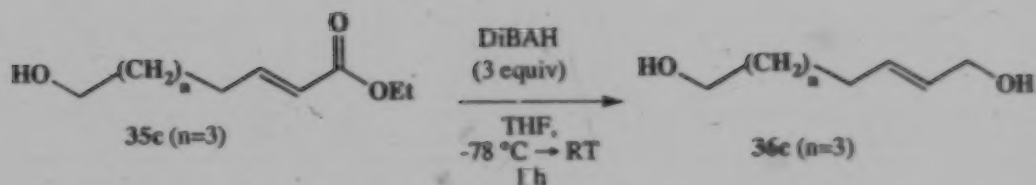
1,1'-Bis(1,3-dimethylindenyl)titanium(III) chloride was prepared by Norman in work that has yet to be published.¹⁹

Experimental



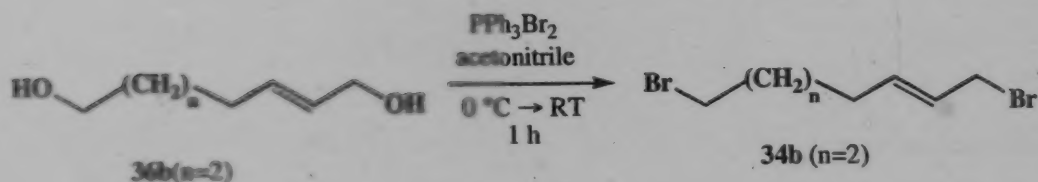
Trans-2-heptene-1,7-diol (36b).²³

In a large Schlenk flask, *trans*-7-hydroxy-hept-2-enoic acid ethyl ester (5.4 g, 31.3 mmol) (note contains about 5% of the *cis* isomer) was dissolved in THF (200 mL). The solution was cooled down to -78 °C and stirred magnetically. A solution of diisobutylaluminumhydride in toluene (1.5 M, 94.1 mmol) was added via dropping funnel over a 3 h period. The solution was then allowed to warm slowly to room temperature over 16 h. The reaction was then quenched by cautious addition of solid Na₂SO₄•10H₂O (10 g), to afford a viscous white paste. Following gravity filtration and washing the filter cake with several portions of THF, the combined organic phase was removed at reduced pressure and the product purified by silica gel flash column chromatography (50/50 ethyl acetate/hexane). 2-Heptene-1,7-diol was isolated as a clear, colourless oil in a yield of 34% (20:1 ratio favoring the *trans* product) ¹H NMR (500 MHz, CDCl₃) δ 5.62 (complex overlapping multiplet, 2H), 4.04 (d, *J* = 6.0 Hz, 2H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.05 (q (dt), *J* = 7.0 Hz, 2H), 1.54 (q (tt), *J* = 7.1 Hz, 2H), 1.43 (q (tt), *J* = 7.1 Hz, 2H).



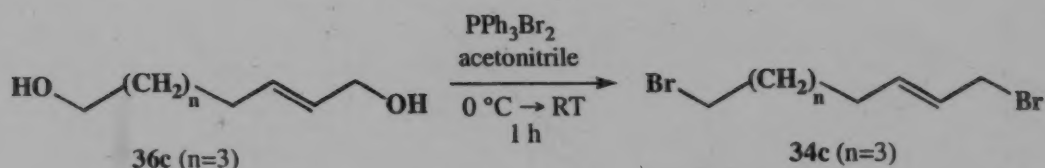
Trans-2-octene-1,8-diol (36c).²⁴

In a large Schlenk flask, *trans*-8-hydroxy-octa-2-enoic acid ethyl ester (6.1 g, 32.7 mmol) (note: contains about 5% of the *cis* isomer) was dissolved in THF (200 mL). The solution was cooled to $-78\text{ }^\circ\text{C}$ and stirred magnetically. A solution of diisobutylaluminumhydride in toluene (1.5 M, 98.5 mmol) was added via dropping funnel over 3 h period. The solution was then allowed to warm slowly to room temperature over 16 h. After this time, the reaction was then quenched by cautious addition of solid $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (10 g), to afford a viscous white paste. Following gravity filtration, and washing the filter cake with several portions of ether, the combined organic phase was removed at reduced pressure and the product purified by silica gel flash column chromatography (50/50 ethyl acetate/hexane). The 2-octene-1,8-diol was isolated as a clear, colourless oil in a yield of 39% (20:1 ratio favoring the *trans* product). ^1H NMR (300 MHz, CDCl_3) δ 5.62 (complex overlapping m, 2H), 4.04 (d, $J = 5.6\text{ Hz}$, 2H), 3.60 (t, $J = 6.5\text{ Hz}$, 2H), 2.42 (broad s, OH, 2H), 2.04 (q (dt), $J = 6.5\text{ Hz}$, 2H), 1.78 (s, OH, 2H), 1.54 (p (tt), $J = 6.6\text{ Hz}$, 2H), 1.35 (complex overlapping m, 4H).



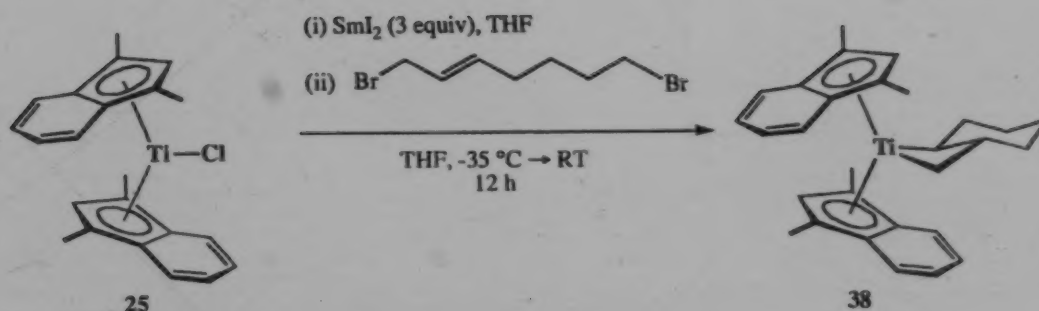
Trans-1,7-dibromo-2-heptene (34b).²³

In a round bottom flask, triphenylphosphine (5.64 g, 21.4 mmol) was dissolved in acetonitrile (25 mL), and the resulting solution was cooled to 0 °C in an ice/water bath. Bromine (3.23 g, 20.2 mmol) was added dropwise via syringe. The ice bath was then removed and the solution was allowed to stand for 20 minutes. At which point 2-heptene-1,7-diol (1.33 g, 10.0 mmol) was added as quickly as possible. After stirring for 1 h, the volume of acetonitrile was reduced in vacuo to about 10 mL and a white precipitate separated from of solution. The precipitate was removed by gravity filtration and the filtrate concentrated under reduced pressure. The resulting orange liquid was passed through a plug of silica gel eluting with 5% ethyl acetate in hexane. The solvents were removed under reduced pressure. The final product, 1,7-dibromo-2-heptene was obtained as a clear, colourless liquid (1.87 g, 81%). ¹H NMR (500 MHz, CDCl₃) δ 5.70 (complex overlapping multiplet, 2H), 3.91 (d, *J* = 7.0 Hz, 2H), 3.60 (t, *J* = 6.8 Hz, 2H), 2.05, q (dt), *J* = 7.2 Hz, 2H), 1.54 (q (tt), *J* = 7.2 Hz, 2H), 1.43 (q (tt), *J* = 7.5 Hz, 2H).). ¹³C{¹H} NMR (125 Hz, CDCl₃), δ 135.6, 127.1, 33.5, 33.2, 32.1, 31.2, 27.3. HRMS *m/z* calcd. For C₇H₁₂⁸¹Br (M-Br): 177.010; found: 177.00992 (53.60%); for C₇H₁₂⁷⁹Br (M⁺-Br): 175.0122; found: 175.0120 (54.70%); for C₇H₁₁ (M-HBr₂): 95.0870; found: 95.0860 (100%)



Trans-1,8-dibromo-2-octene (34c).

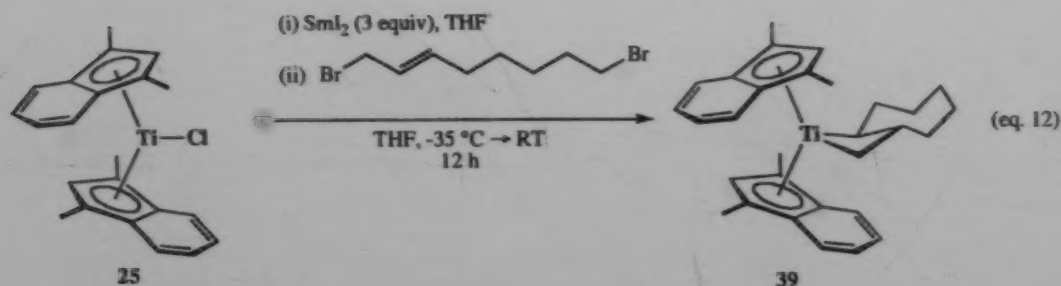
In a round bottom flask, triphenylphosphine (4.0 g, 15.1 mmol) was dissolved in acetonitrile (25 mL) and the resulting solution was cooled to 0 °C in a ice/water bath. Bromine (2.38 g, 14.9 mmol) was added dropwise via syringe. The ice bath was then removed and the solution was allowed to stand for 20 min. At this point 2-heptene-1,7-diol (1.1 g, 7.63 mmol) was added as quickly as possible. After stirring for 1 h, the volume of acetonitrile was reduced in vacuo to about 10 mL and a white precipitate separated from solution. The precipitate was removed by gravity filtration and the filtrate was then concentrated under reduced pressure. The resulting orange oil was passed through a plug of silica gel eluting with 5% ethyl acetate in hexane. The solvents were removed under reduced pressure. The final product, 1,8-dibromo-2-octene, was obtained as a clear colourless liquid (1.61 g, 78%). ¹H NMR (300 MHz, CDCl₃) δ 5.71 (complex overlapping multiplet, 2H), 3.93 (d, *J* = 6.6 Hz, 2H), 3.60 (t, *J* = 6 Hz, 2H), 2.04 (q (dt), *J* = 6.4 Hz, 2H), 1.84 (p, *J* = 6.7 Hz, 2H), 1.41 (complex overlapping m, 4H). ¹³C{¹H} NMR (125 MHz, CDCl₃), δ 135.9, 126.7, 33.6, 33.3, 32.5, 31.8, 27.9, 27.6. HRMS *m/z* calcd. For C₈H₁₄⁸¹Br₂ (M⁺): 271.9421; found: 271.9417 (0.84%); for C₈H₁₄⁷⁹Br⁸¹Br (M⁺): 269.9441; found: 271.94178 (1.74%) ; for C₈H₁₄⁷⁹Br₂ (M⁺): 267.9462; found: 267.9458 (0.88%); for C₈H₁₃ (M-HBr₂): 109.1017; found: 109.1017 (100%)



1,1'-[bis(1,3-dimethylindenyl)]titanabicyclo[4.2.0]octane (38).

In a small vial in the dry box, 1,1'-bis(1,3-dimethylindenyl)titanium(III) chloride¹⁹ (88.3 mg, 0.239 mmol) was dissolved in a solution of SmI₂ (7.4 mL, 0.1 M, THF). The solution was placed in the drybox freezer at -35 °C. A second vial was charged with 1,7-dibromo-2-heptene (61 mg, 0.238 mmol) and THF (1 mL) and also placed in the drybox freezer. After 1 h the two solutions were mixed and maintained at -35 °C for one additional hour. The reaction mixture was then stirred and allowed to warm up to room temperature over 12 h, affording a dark brown solution and a pale yellow precipitate. The solution was filtered through celite, and the solvent was removed under reduced pressure. The resulting red solid was triturated into pentane and passed again through a small plug of celite. Removal of pentane in vacuo yielded 1,1'-[bis(1,3dimethylindenyl)]-titanabicyclo[4.2.0]octane **38** (71.3 mg, 69.5%) as a red solid. ¹H NMR (300 MHz, C₆D₆) 7.24 (d, *J* = 12 Hz, 1H) 7.1-6.8 (complex overlapping multiplet, 7H), 5.01 (s, 1H), 3.82 (s, 1H), 2.31 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 1.98 (m, 1H), 1.96 (m, 1H), 1.87 (m, 1H), 1.68 (m, 1H), 1.67 (m, 1H), , 1.44 (m, 1H), 1.30 (m, 1H), 1.98 (m, 1H), 1.05 (m, 1H) 0.4 (m, 1H), -1.36 (t, *J* = 11.4 Hz, 1H), -1.88 (p, *J* = 10.8 Hz, 1H). ¹³C{¹H} NMR (125 MHz, C₆D₆) δ 126.8, 126.7, 125.3, 125.0, 124.0, 123.6, 123.5, 122.8, 122.5,

122.5, 122.1, 122.0, 108.7, 107.9, 107.7, 105.4, 38.0, 33.2, 32.1, 26.9, 13.2, 12.7, 12.1, 11.9; HMQC (600 MHz, C_6D_6) δ 119.8 $\leftrightarrow$ δ 5.9; δ 117.9 (C) $\leftrightarrow$ δ -1.36 (H); δ 116.9 $\leftrightarrow$ δ 3.82; δ 78.5 (C) $\leftrightarrow$ δ 1.96, δ 1.44; δ 18.1 (C) $\leftrightarrow$ δ -1.88 (H). Detailed assignments are discussed in the results section. HRMS m/z calcd. For $C_{22}H_{22}Ti(M-C_7H_{12})$: 334.1198; found: 334.1983 (2.15%).



1,1'-[Bis(1,3-dimethylindenyl)]titanabicyclo[5.2.0]nonane (39).

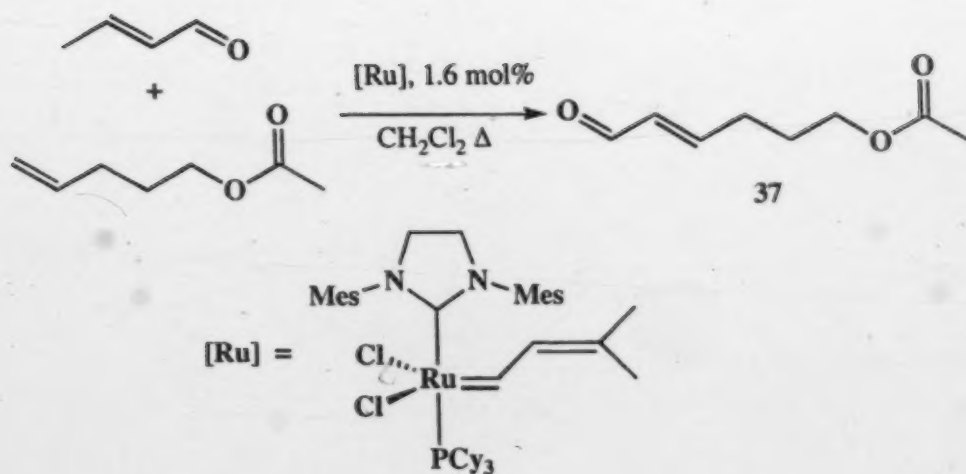
In a small vial in the drybox,, bis(1,3-dimethylindenyl)titanium(III) chloride¹⁹ (87.6 mg, 0.236 mmol) was dissolved in a solution of SmI_2 in THF (7.4 mL, 0.1 M, THF). This solution was placed in the drybox freezer at $-35^\circ C$. A second vial was charged with 1,7-dibromo-2-octene (61 mg, 0.238 mmol) in THF (1 mL) and placed in the drybox freezer. After 1 hour the solutions were mixed and maintained at $-35^\circ C$ for one additional hour. The reaction mixture was then stirred magnetically and allowed to warm up to room temperature over 12 h, affording a dark brown solution and a yellow precipitate. The solution was filtered through celite and the solvent was removed under reduced pressure. The remaining red precipitate was triturated with pentane and passed again through a small plug of celite. Removal of pentane in vacuo yielded 6-[bis(1,3-dimethylindenyl)]titanabicyclo[4.2.0]nonane (78.6 mg, 75%) as a red solid. ^1H NMR (300 MHz, C_6D_6) 7.39 (d, $J = 12$ Hz, 1H) 7.2-6.8 (complex overlapping multiplet, 7H), 5.15 (s,

1H), 3.29 (s, 1H), 2.44 (t, $J = 9$ Hz, 1H), 2.22 (s, 3H), 2.14 (s, 3H), 2.09 (s, 3H), 2.00 (m, 1H), 1.97 (s, 3H), 1.89 (t, $J = 9$ Hz, 1H), 1.72 (m, 1H), 1.68 (m, 1H), 1.58 (m, 1H), 1.50 (m, 1H), 1.41 (m, 1H), 1.23 (m, 2H), 0.41 (m, 1H), -0.98 (dq, $J = 10.5$ Hz, 6 Hz, 1H), -1.88 (ddd, $J = 10.5$ Hz, 10.6 Hz, 5 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6), δ 127.2, 126.7, 125.6, 124.5, 124.2, 124.0, 123.7, 123.4, 123.1, 122.7, 122.6, 122.3, 121.5, 116.7, 111.3, 105.6, 105.0, 38.0, 34.1, 32.2, 29.7, 26.9, 18.4, 13.3, 12.9, 12.1, 11.8; HMQC (600 MHz C_6D_6); δ 104.7 (C) $\leftrightarrow$ -1.76 (H_1); δ 87.1 (C) $\leftrightarrow$ 2.44, 1.89; δ 18.3 (C) $\leftrightarrow$ -0.98 (H).

Detailed assignments are discussed in the results section. HRMS m/z calcd. For

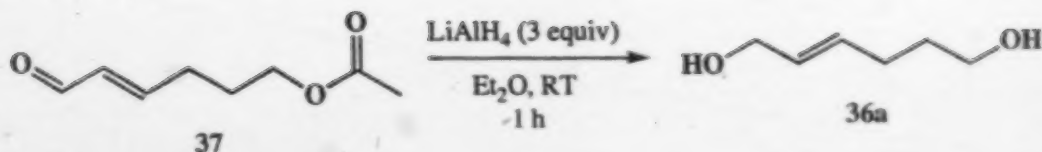
$\text{C}_{22}\text{H}_{22}\text{Ti}(\text{M}-\text{C}_8\text{H}_{14})$: 334.1200; found: 334.12068 (18.00%); for $\text{C}_8\text{H}_{14}(\text{M}-$

$\text{C}_{22}\text{H}_{22}\text{Ti})$: 110.10955; found: 110.10982 (28.70%).



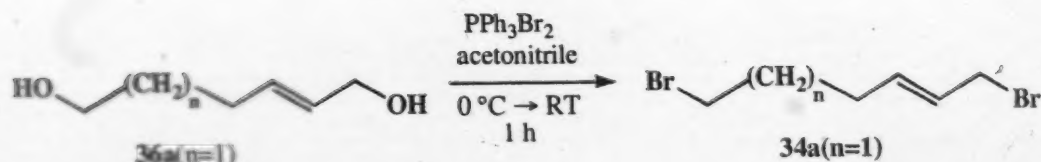
Trans-2-hexenal-6-acetate (37).

A 100 mL round bottom flask was charged with 4-pentenyl acetate (2.8 g, 21.8 mmol), distilled crotonaldehyde (7.5 g, 109 mmol), tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV)dichloride²² (165 mg, 0.34 mmol) and dried degassed dichloromethane (35 mL). The reaction mixture was maintained at reflux for 48 h. The solvent was then removed under reduced pressure to afford a brown oil. The oil was purified by silica gel column chromatography (50/50 hexane/ethyl acetate). The final product, *trans*-2-hexenal-6-acetate (70%), was obtained as a colourless oil. A small amount (~5%) of *cis* product could also be detected by ¹H NMR spectroscopy. ¹H NMR (300 MHz, CDCl₃) δ 9.42 (d, *J* = 7 Hz, 1H), 6.80 (dt, *J*₁ = 6.0 Hz, *J*₂ = 14 Hz, 1H), 6.05 (ddt, *J*₁ = 6 Hz, *J*₂ = 7 Hz, *J*₃ = 1 Hz, 1H), 4.04 (t, *J* = 6 Hz, 2H), 1.54 (q (tt), *J* = 7 Hz, 2H), 2.0 (s, 3H) 1.43 (p (tt), *J* = 7 Hz, 2H). This product was carried on without further characterization.



Trans-2-hexene-1,6-diol (36a).

A Schlenk flask was charged lithium aluminum hydride (0.95 g, 25 mmol) and diethyl ether (25 mL). To this solution, *trans*-2-hexenal-6-acetate (1.2 g, 8.33 mmol) was then added in small portions at room temperature with vigorous stirring. After 1 hour the excess lithium aluminum hydride was carefully quenched by slow addition of water (1 mL), followed by NaOH (1 mL, 1.0 M), and then water (3 mL). The solution was then filtered to remove the white granular precipitate and the solvent was removed under reduced pressure to furnish a yellow oil. The oil was purified by silica gel flash column chromatography (ethyl acetate), yielding *trans*-2-hexene-1,6-diol (0.44 g, 63%) as a colourless oil. ^1H NMR (300 MHz, CDCl_3) δ 5.62 (complex overlapping m, 2H), 4.03 (d, $J = 5$ Hz, 2H), 3.60 (t, $J = 6$ Hz, 2H), 2.05, q (dt), $J = 7$ Hz, 2H), 1.62 (q (tt), $J = 7$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 132.3, 129.6, 63.4, 62.2, 31.9, 28.5. MS m/z calculated for $\text{C}_6\text{H}_{12}\text{O}_2$ (M^+): 116.08383; found 116.08221 (1.3%); calculated for ($M - \text{H}_2\text{O}$): 98.07317; found 98.07276 (93.9%).



***Trans*-1,6-dibromo-2-hexene. 34a**

In a round bottom flask, triphenylphosphine (1.14 g, 4.34 mmol) was dissolved in acetonitrile (15 mL), and the resulting solution cooled to 0 °C in a ice/water bath.

Bromine (0.66 g, 4.13 mmol) was added dropwise via syringe. The ice bath was then removed and the solution was allowed to stand for 20 min. At this point, 2-heptene-1,7-diol (0.24 g, 2.07 mmol), was added as quickly as possible. After stirring for 1 h, the volume of acetonitrile was reduced in vacuo to about 10 mL and a white precipitate separated from solution. The precipitate was removed by gravity filtration and the filtrate concentrated under reduced pressure, and the resulting orange liquid was passed through a plug of silica gel eluting with 5% ethyl acetate in hexane. The solvents were removed under reduced pressure. The final product, 1,6-dibromo-2-hexene, was obtained as a clear, colourless liquid in a yield of (0.37 g, 76 %). ¹H NMR (300 MHz, CDCl₃) δ 5.72 (complex overlapping m, 2H), 3.92 (d, *J* = 6.5 Hz, 2H), 3.38 (t, *J* = 6 Hz, 2H), 2.21 (q (dt), *J* = 6.5 Hz, 2H), 1.84 (p, *J* = 7 Hz, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃), δ 134.1, 127.9, 32.8, 32.7, 31.6, 30.3.

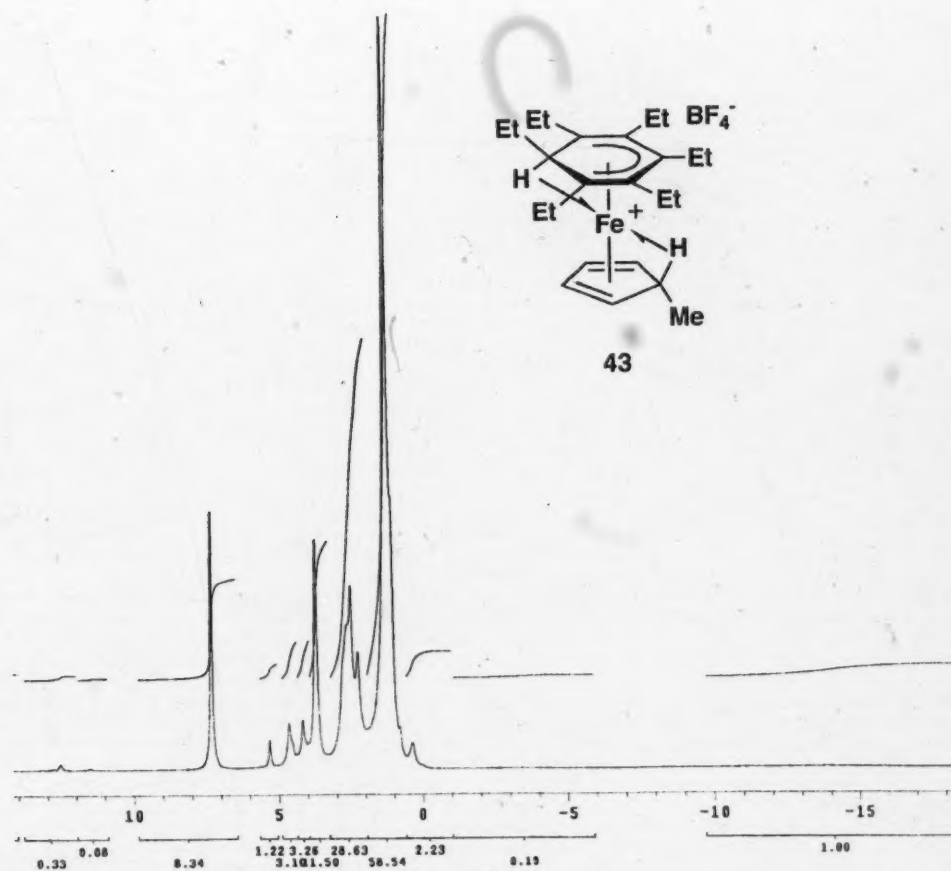
2.4 References:

1. (a) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. (b) Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619.
2. Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.
3. Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.
4. (a) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Green, J. *Chem. Soc. Rev.* **1998**, *27*, 263.
5. Tjaden, E. B.; Casty, G. L.; Stryker, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 9814.
6. Casty, G. L. Ph. D. Dissertation, Indiana University, 1994.
7. Carter, C. A. G. Ph. D. Dissertation, University of Alberta 1994.
8. Casty, G. L.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7814.
9. Wardell, J. L. In *Comprehensive Organometallic Chemistry Vol. 2*. Wilkinson, G. ed. Pergamon Press, New York, 1982, p. 910 and references therein.
10. Giese, B. *Radicals in Organic Synthesis: Formations of Carbon-Carbon Bonds*. Pergamon, Oxford, 1986.
11. (a) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986 and references therein. (b) RajanBabu, T. V.; Nugent, W. A.; Beattie, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 6408. (c) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1989**, *111*, 8561. (d) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1989**, *111*, 4525.
12. (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. (b) Review: Imamoto, T. *Lanthanides in Organic Synthesis*; Academic Press: San Diego, 1994.
13. (a) Martin, H. A.; Lemaire, P. J.; Jellinek, F. J. *Organomet. Chem.* **1968**, *14*, 149. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Nakamura, A. *Chem. Lett.*

- 1981, 671. Mashima, K.; Yasuda, H.; Asami, K.; Nakamura, A. *Chem. Lett.* **1983**, 219. (c) Blenkins, J.; de Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, 218, 383. (d) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, 279, 281. (e) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 829, and references therein. (f) Larson, E. J.; van Dort, P. C.; Lakanen, J. R.; O'Neill, D. W.; Pederson, L. M.; McCandless, J. J.; Silver, M. E.; Russo, S. O.; Huffman, J. D. *Organometallics* **1988**, 7, 1183. Vance, P. J.; Prins, T. J.; Hauger, B. E.; Silver, M. E.; Wemple, M. E.; Pederson, L. M.; Kort, D. A.; Kannisto, M. R.; Geerligs, S. J.; Kelly, R. S.; McCandless, J. J.; Huffman, J. D.; Peters, D. G. *Organometallics* **1991**, 10, 917. (g) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1993**, 115, 2083.
14. Carter, C. A. G.; McDonald, R.; Stryker, J. M. *Organometallics* **1999**, 18, 820.
15. Smith, J. A.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, 173, 175. (b) Nifant'ev, I. E.; Butakvo, K. A.; Aliev, Z. G.; Urazovskii, I. F. *Organometallic Chemistry in the USSR* **1991**, 4, 622.
16. Costa, E. M.; Stryker, J. M. Unpublished results.
17. Greidanus, G., C. A. G. Ph. D. Dissertation, University of Alberta, **2001**.
18. Greidanus-Strom, G.; McDonald, R.; Stryker, J. M. *Organometallics* **2001**, 20, 2492
19. Norman, J.; Stryker, J. M. Unpublished results.
20. Carter, C. A. G.; Greidanus, G.; Chen, J.-X.; Stryker, J. M. *J. Am. Chem. Soc.* **2001**, 123, 8872.
21. Takacs, J. M.; Helle, M. A.; Seely, F. L. *Tetrahedron Lett.* **1986**, 27, 1257.
22. Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, 122, 3783.
23. Colonge, J. *Bull. Soc. Chim. Fr.* **1963**, 551.
24. Klok, R.; Moehlmann, W. M. M.; van der Wolf, L.; Pabon, H. J. *J. R. Neth. Chem. Soc.* **1980**, 99, 132.

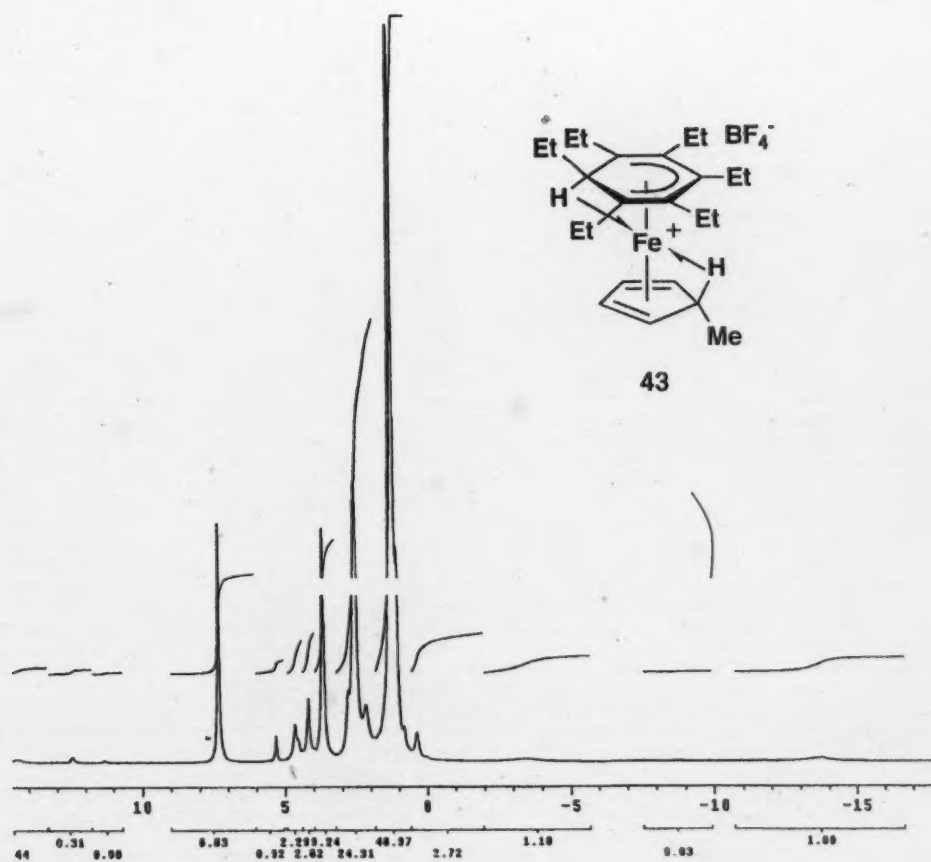
Appendices

Appendix 1 Protonation of Complex 23 ^1H NMR spectra (CD_2Cl_2)



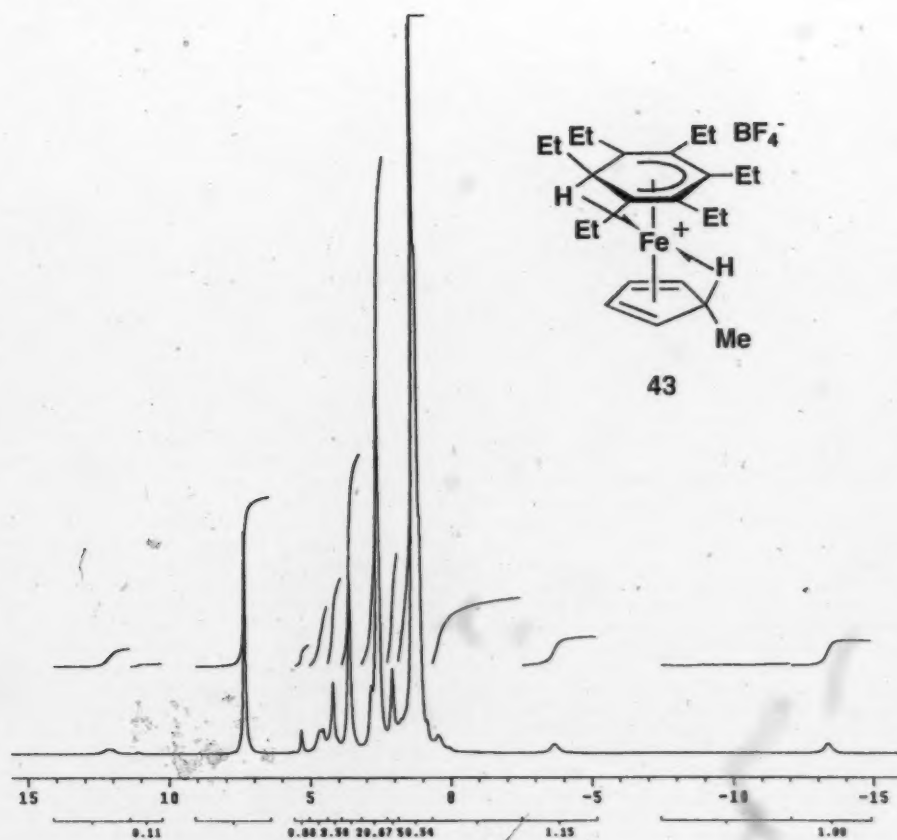
Complex 43 at -80°C ^1H NMR spectrum (CD_2Cl_2)

Appendix 1 (continued)



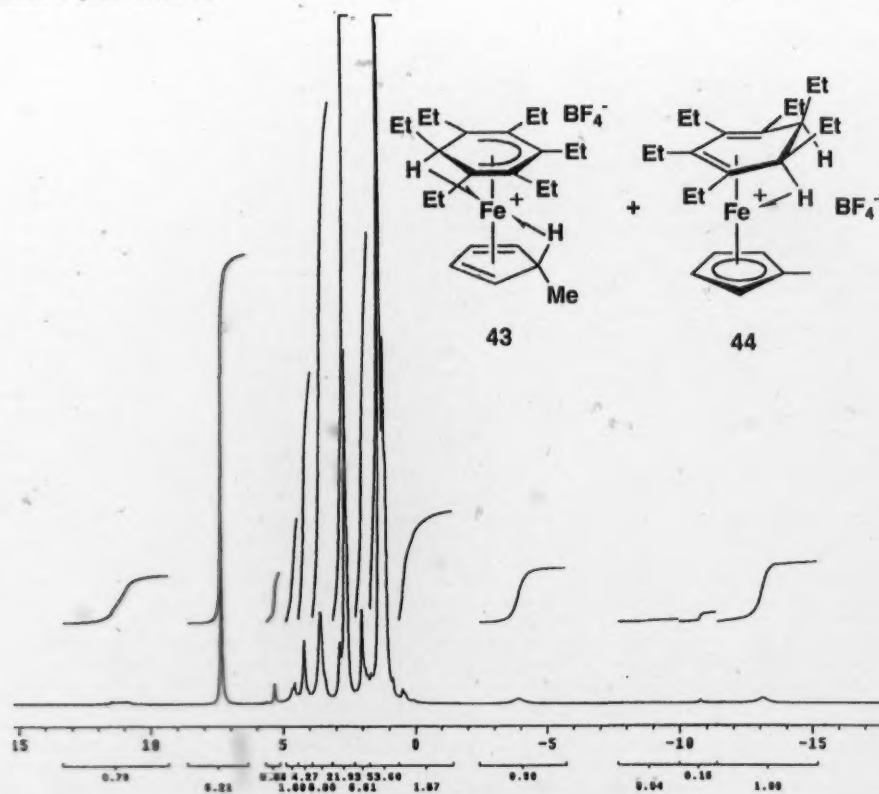
Complex 43 at $-60\text{ }^\circ\text{C}$ ^1H NMR spectrum (CD_2Cl_2)

Appendix 1 (continued)



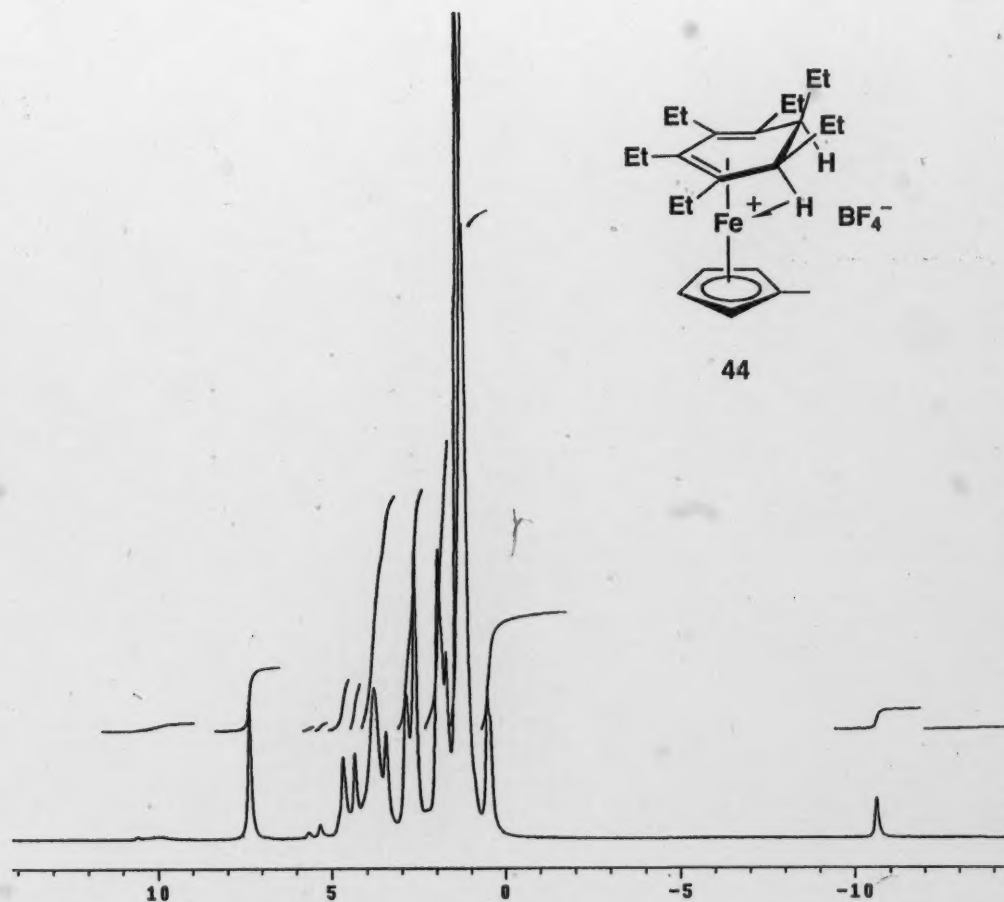
Complex 43 at -40°C ^1H NMR spectrum (CD_2Cl_2)

Appendix 1 (continued)



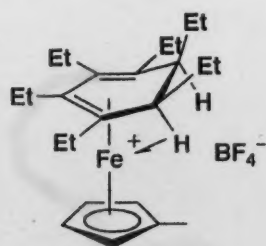
Complex 43 and 44 at $-20\text{ }^\circ\text{C}$ ^1H NMR spectrum (CD_2Cl_2)

Appendix 1 (continued)

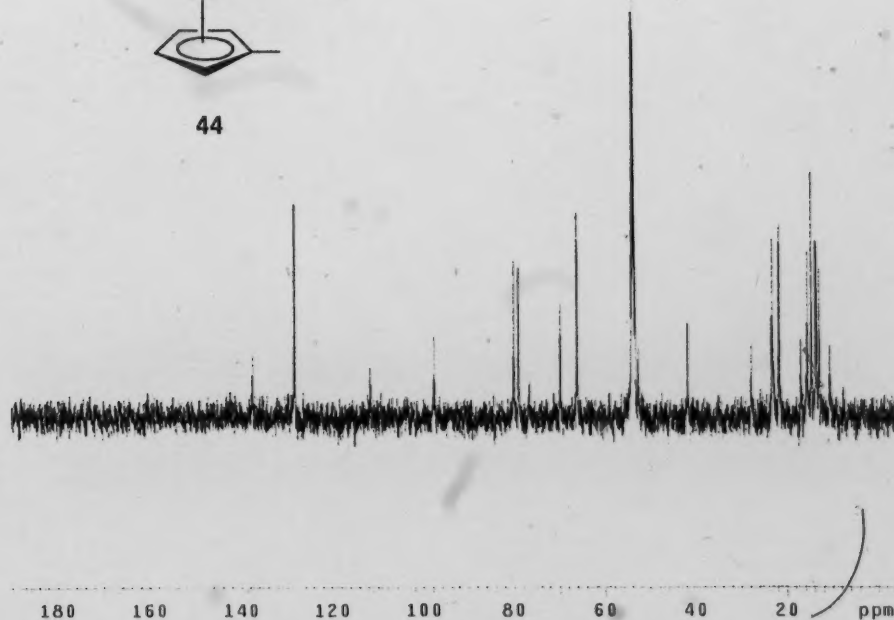


Complex 44 at 20°C ^1H NMR spectrum (CD_2Cl_2)

Appendix 1 (continued)

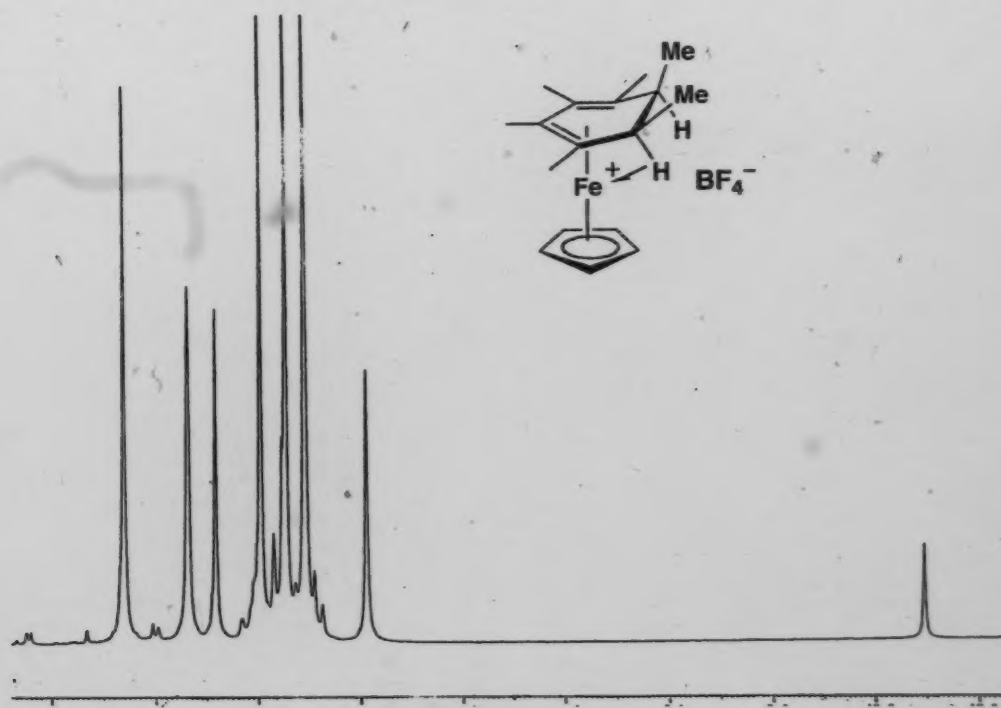


44



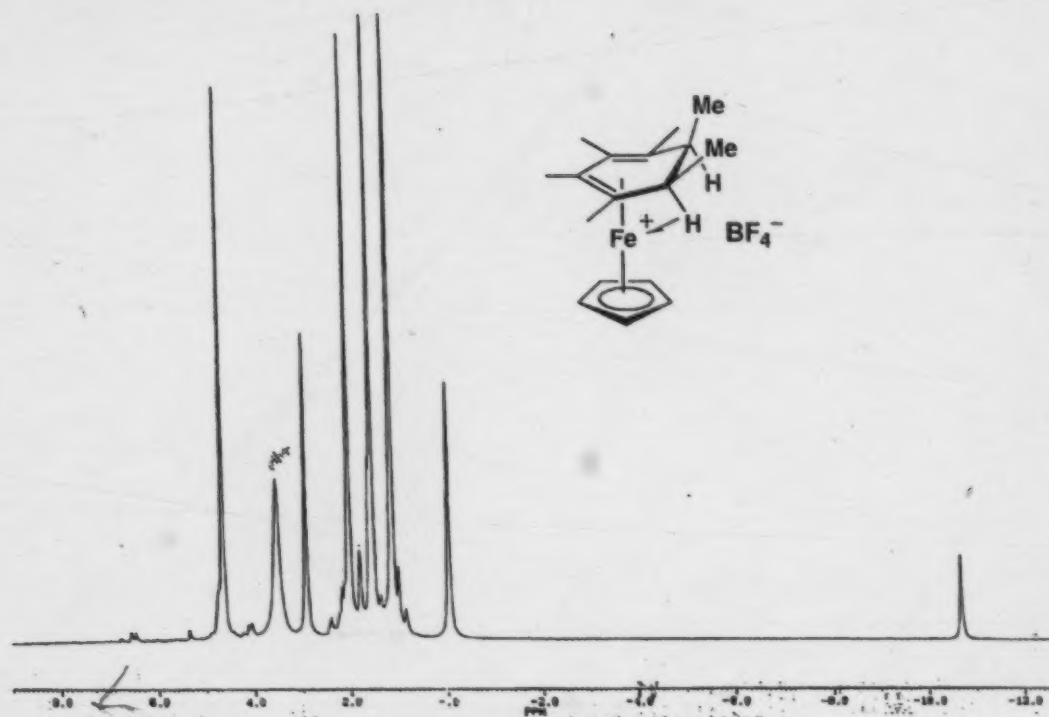
Complex 43 at 20 °C $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2)

Appendix 2 Protonation of Complex 23 NMR spectra



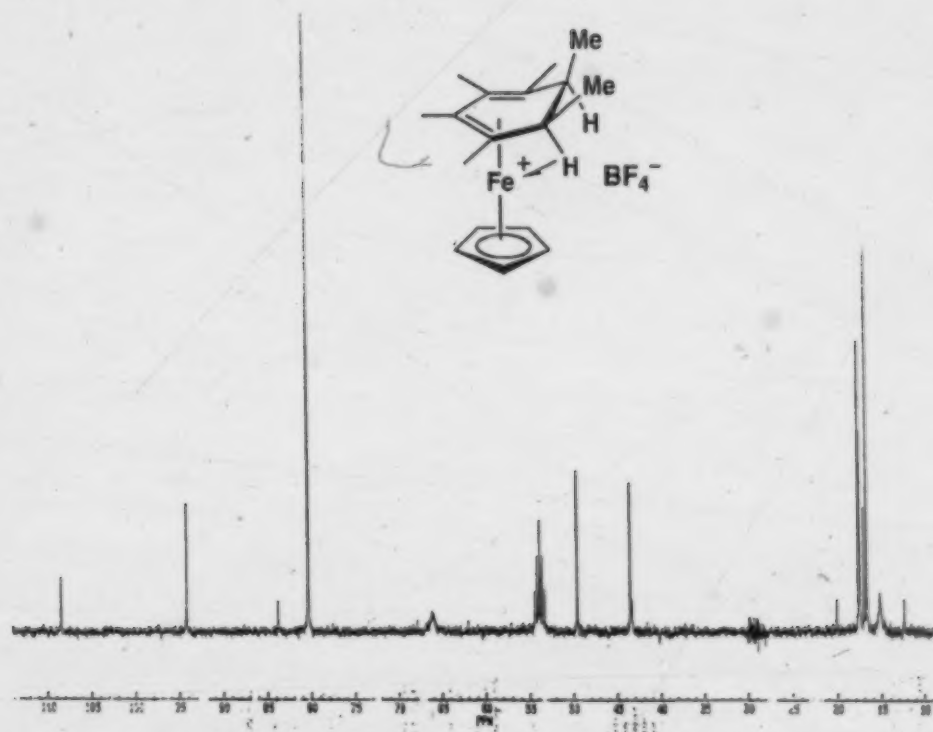
Complex 36 at $-100\text{ }^\circ\text{C}$ ^1H NMR spectrum (CD_2Cl_2)

Appendix 2 (continued)



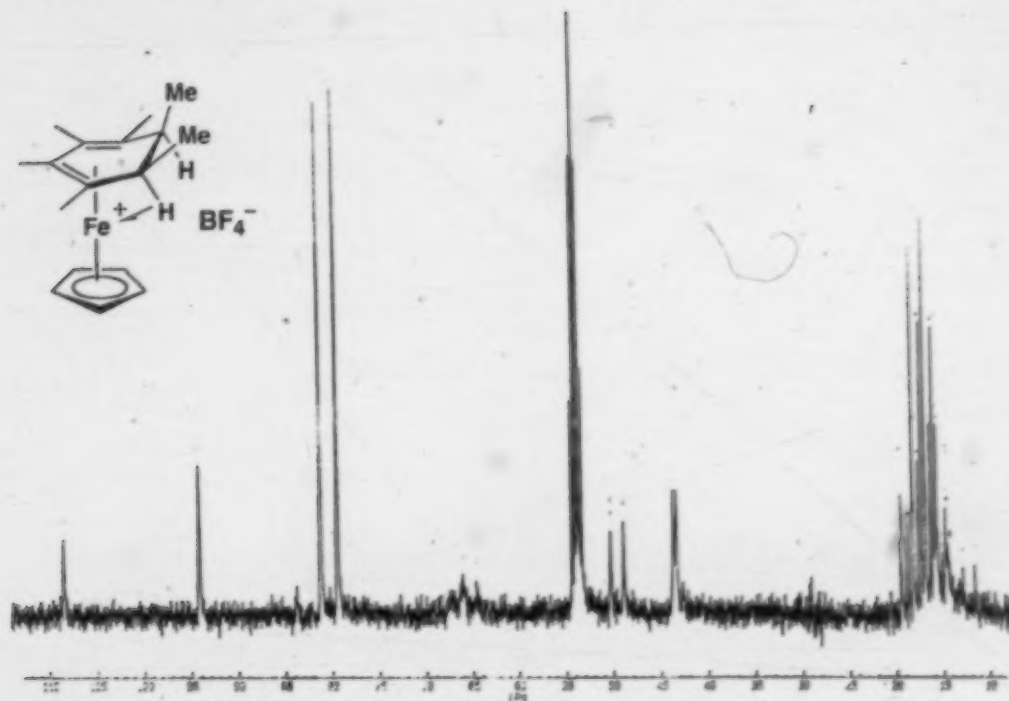
Complex 36 at -20°C ^1H NMR spectrum (CD_2Cl_2)

Appendix 2 (continued)



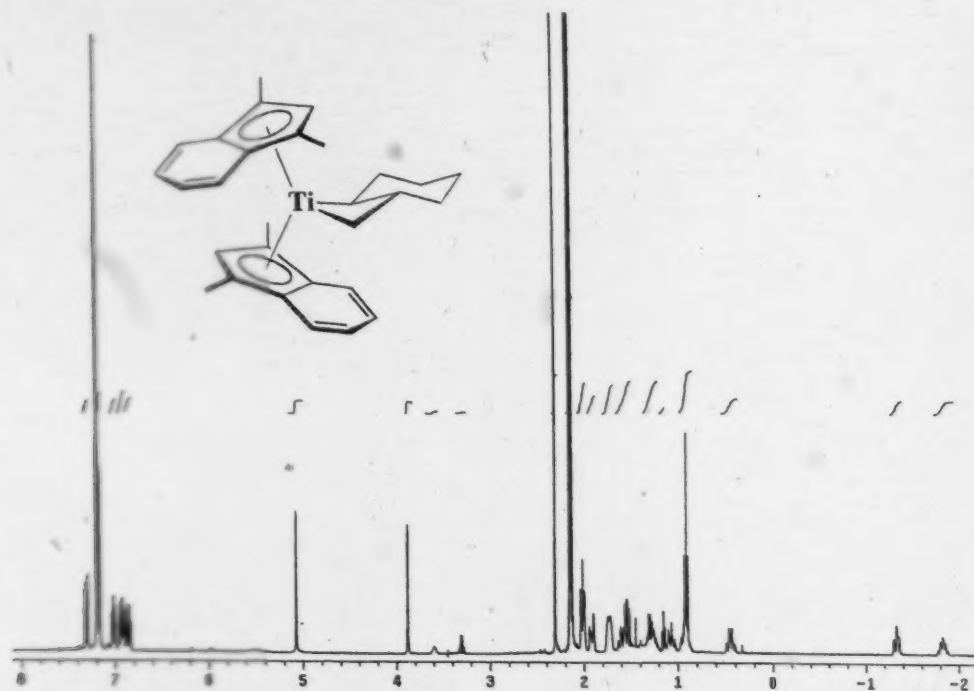
Complex 36 at $-40\text{ }^{\circ}\text{C}$ $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2)

Appendix 2 (continued)



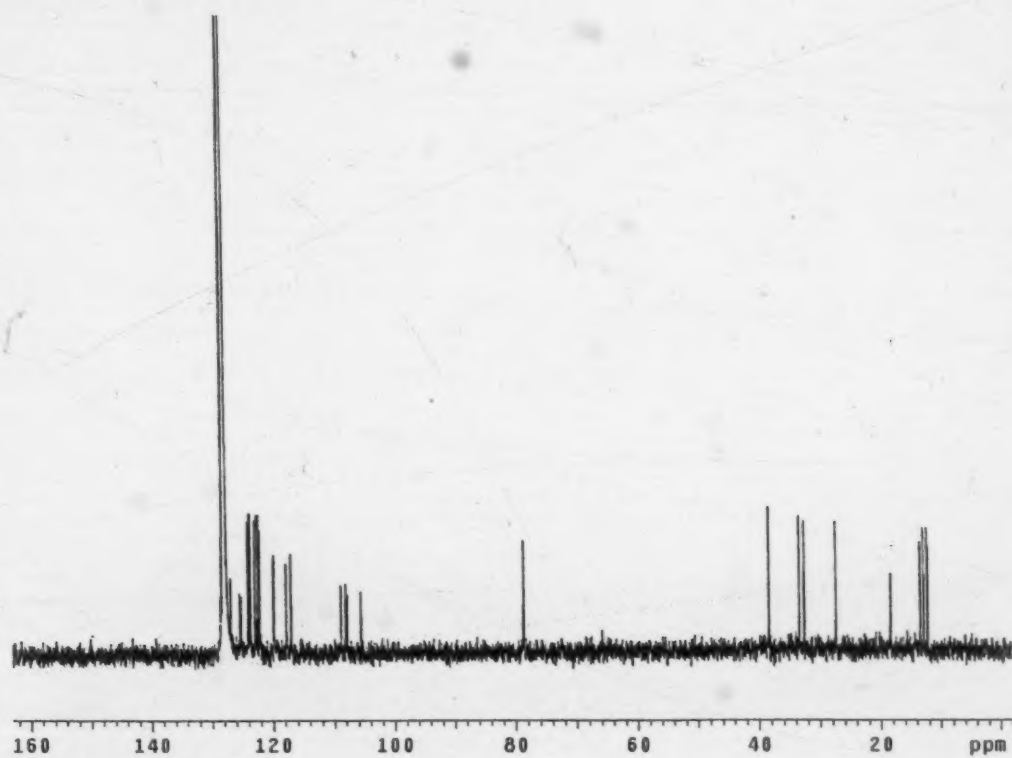
Complex 36 at -40°C ^{13}C [^1H coupled] NMR spectrum (CD_2Cl_2)

Appendix 3 NMR spectra of titanium complex 38



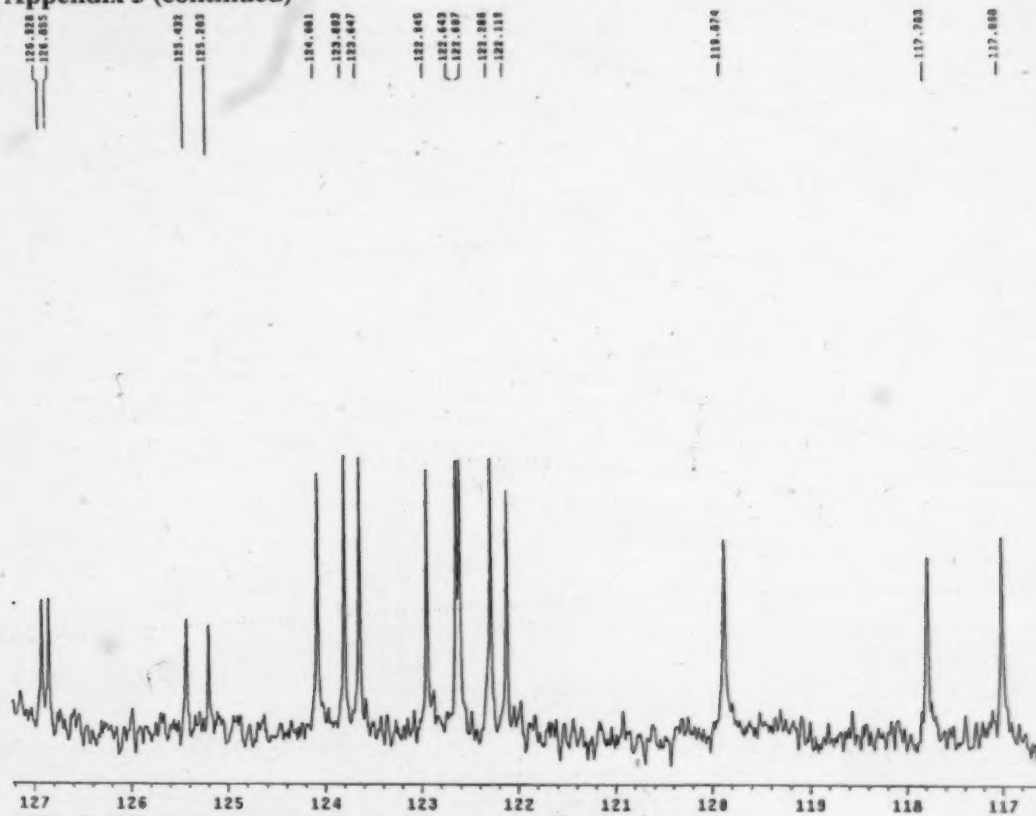
Complex 38 ^1H NMR spectrum (C_6D_6)

Appendix 3 (continued)



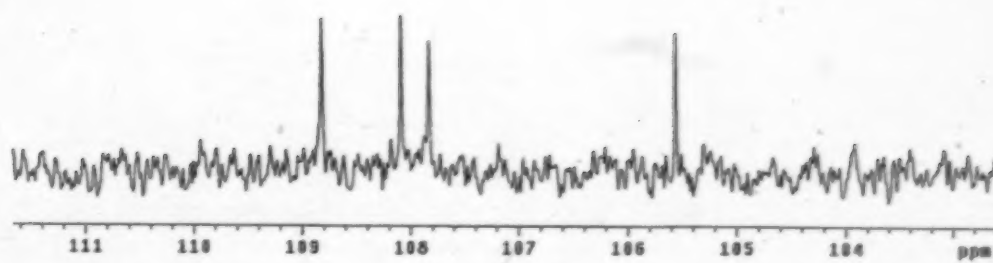
Complex 38 ^{13}C [^1H] NMR spectrum (C_6D_6)

Appendix 3 (continued)



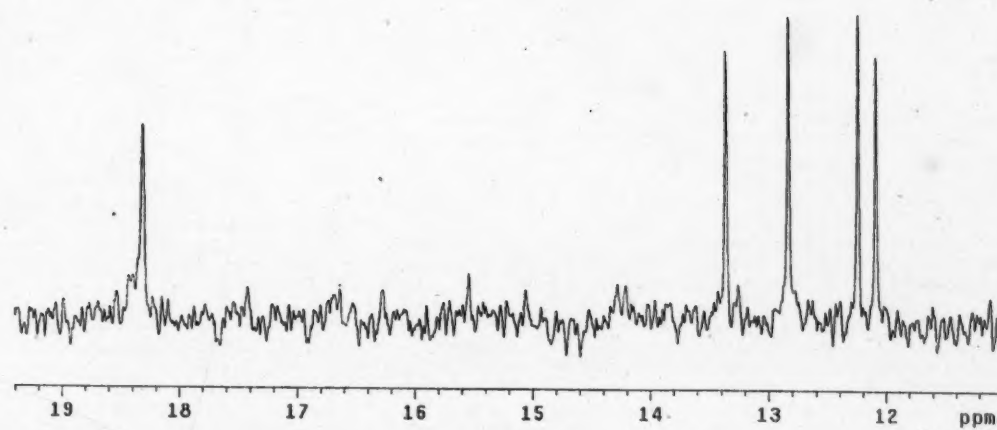
Complex 38 $^{13}\text{C}[^1\text{H}]$ NMR spectrum (expansion) (C_6D_6)

Appendix 3 (continued)



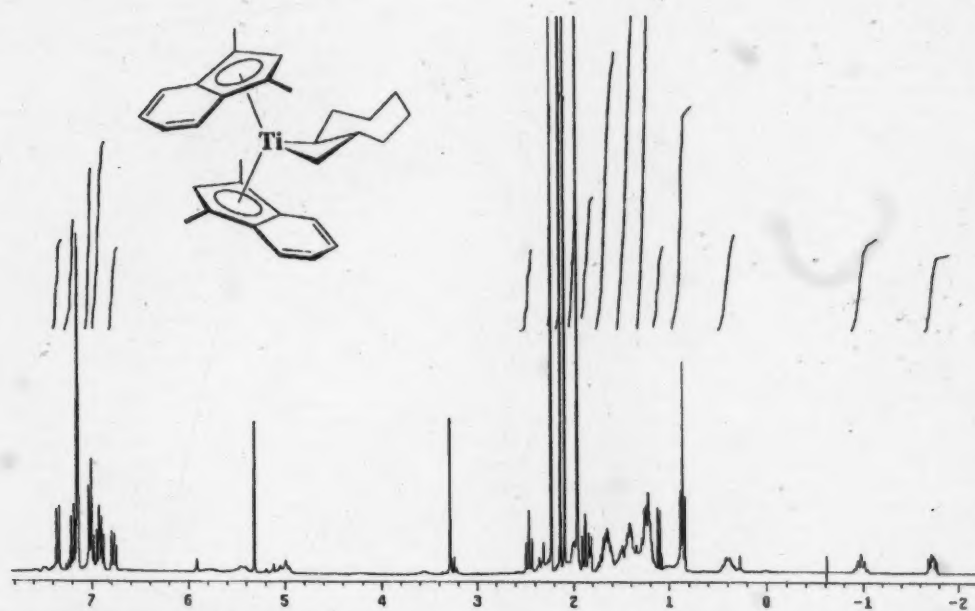
Complex 38 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (expansion) (C_6D_6)

Appendix 3 (continued)



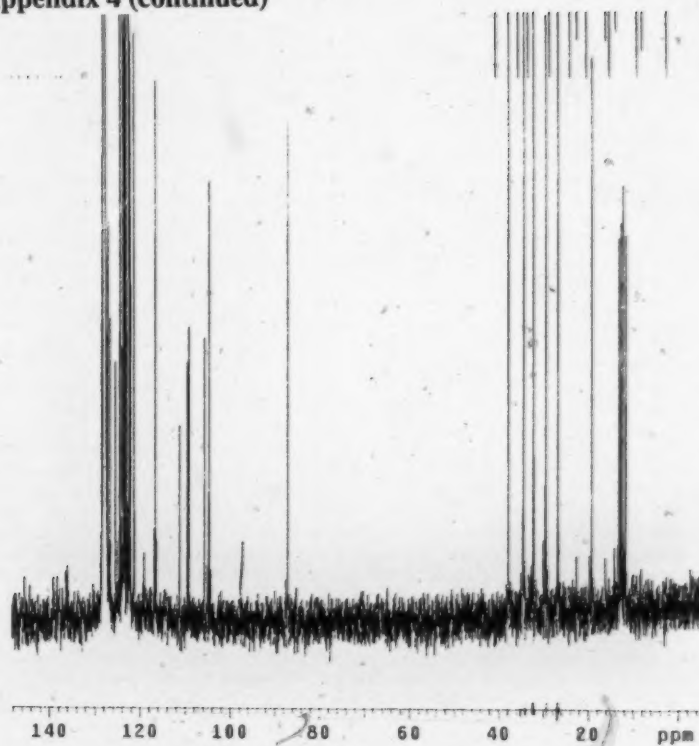
Complex 38 ^{13}C [^1H] NMR spectrum (expansion) (C_6D_6)

Appendix 4 NMR spectra of titanium complex 39



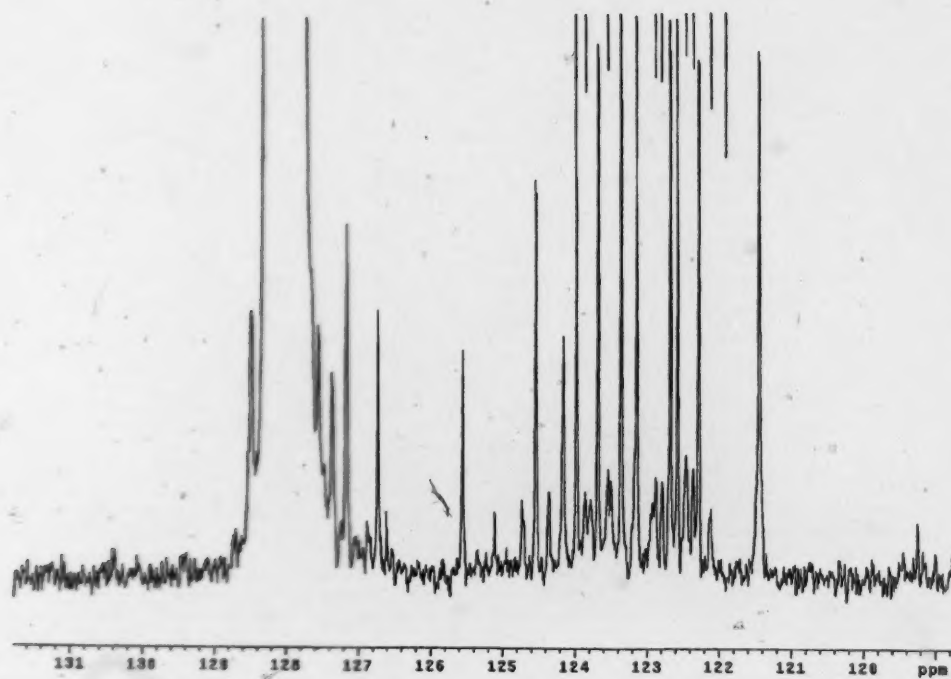
Complex 39 ^1H NMR spectrum (C_6D_6)

Appendix 4 (continued)



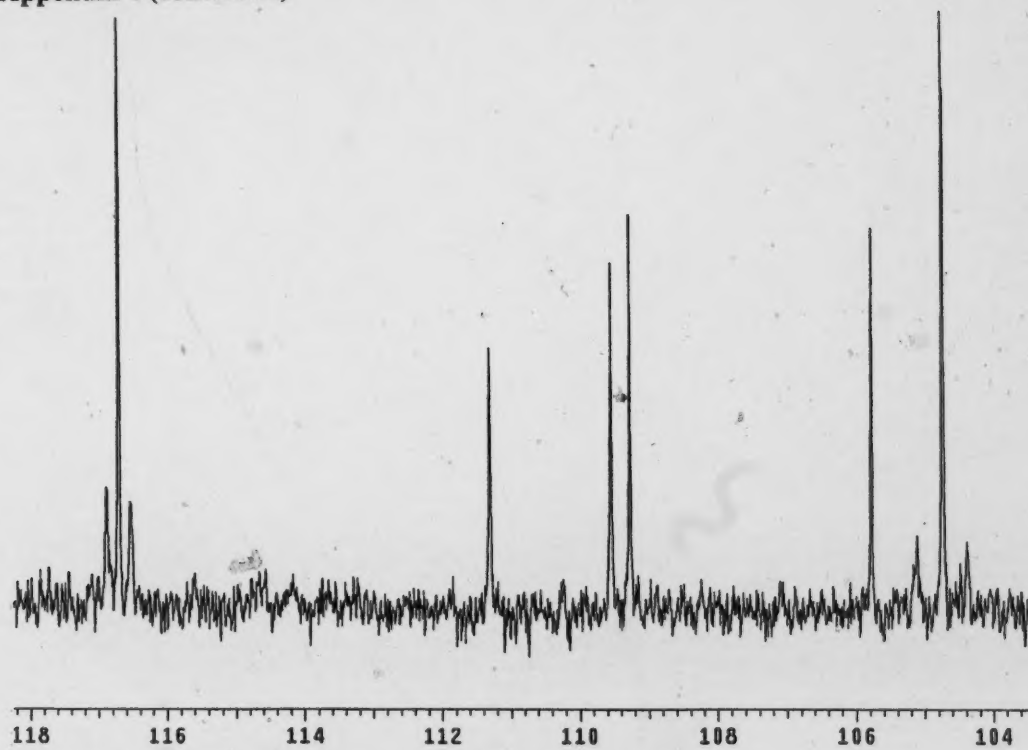
Complex 39 ^{13}C [^1H] NMR spectrum (C_6D_6)

Appendix 4 (continued)



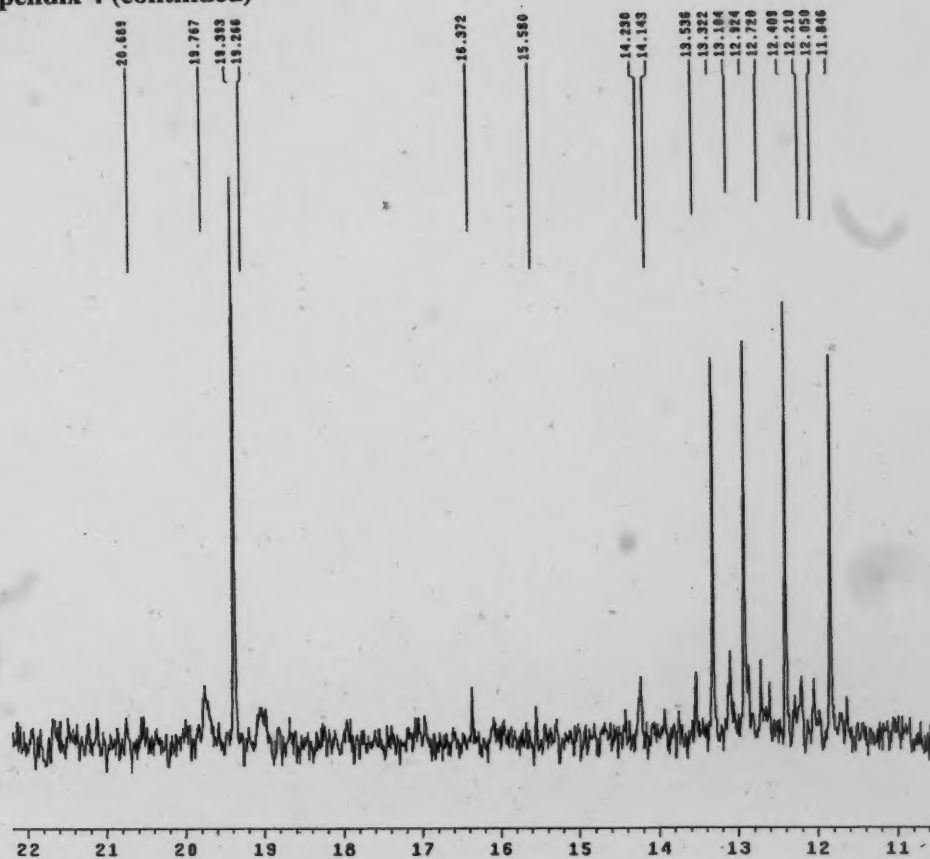
Complex 39 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (expansion) (C_6D_6)

Appendix 4 (continued)



Complex 39 ^{13}C [^1H] NMR spectrum (expansion) (C_6D_6)

Appendix 4 (continued)



Complex 39 $^{13}\text{C}[^1\text{H}]$ NMR spectrum (expansion) (C_6D_6)